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RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

A REPORT TO

OFFICE OF NAVAL RESEARCH

CONTRACT NOnr-2655(00), ARPA ORDER NO. 170-61
PROJECT CODE 9100

OCTOBER 1963
COPY NO. 12

CHEMICAL PRODUCTS DIVISION
AEROJET-GENERAL CORPORATION
AZUSA, CALIFORNIA

(0235)

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October 1963, Report No. 2730

RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

By:

K. Baum
F. J. Gerhart
A. F. Graefe
V. Grakauskas
A. Remanick
[redacted]

Analytical Support:

C. L. Deuel
K. Inouye
D. I. Matson
H. Nelson
H. W. Pust

A Report To

OFFICE OF NAVAL RESEARCH

Contract NOnr-2655(00), ARPA Order [redacted] 170-61
Project Code 9100

AEROJET-GENERAL CORPORATION

A Subsidiary of the General Tire & Rubber Company

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This report summarizes the research carried out under Contract NOnr-2655(00), ARPA Order No. 170-61, Project Code 9100, during the period 1 September 1962 through 30 September 1963.

AEROJET-GENERAL CORPORATION

Louis R Rapp

L. R. Rapp, Manager
Chemical Products Division

ABSTRACT

During the past year, emphasis has continued ~~to be~~ on studies of the reactions of difluoramine and on the fluorination of nitrogenous materials in aqueous solutions, with the aim of producing new types of high-energy compounds. The chemical reactivity of these materials was examined. Work was also carried out to prepare inorganic NF oxidizers. This area has included the preparation of fluorammonium salts and the characterization of a reported complex of azine fluoride and potassium fluoride.

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I. INTRODUCTION

This report summarizes the carried out research under Contract NOnr-2655(00), ARPA Order No. 170-61, Project Code 9100, during the period 1 September 1962 through 30 September 1963. The work performed from 1 September 1962 to 31 May 1963 has been reported in Aerojet-General Quarterly Reports 0235-01-15, -16, and -17, and will be summarized here and referenced. Experimental details will be included only for the period 1 June to 30 September 1963. This work is a direct continuation of the research under Contracts NOnr-2655(00) and N7onr-462, Task Order 1, which has been summarized in Aerojet-General Reports 1162, 1318, 1509, 1685, 1877, 2099, and 2381.

During the past year, emphasis has continued to be on studies of the reactions of difluoramine and on the fluorination of nitrogenous materials in aqueous solutions, with the aim of producing new types of high-energy compounds. The chemical reactivity of these materials was examined. Work was also carried out to prepare inorganic NF oxidizers. This area has included the preparation of fluorammonium salts and the characterization of a reported complex of azine fluoride and potassium fluoride.

II. TECHNICAL DISCUSSION

A. REACTIONS OF DIFLUORAMINE (K. Baum, F. J. Gerhart)

1. Discussion

a. Reaction of Acetylenes with Difluoramine

The boron trifluoride complex of phosphoric acid was previously used as a catalyst for the addition of difluoramine to 3-hexyne.* Two products which were extracted from the reaction mixture with pentane were identified as 3-hexanone and 3,3-bis(difluoramino)hexane. Subsequently another

*Aerojet-General Report 2381, October 1962, p. 12 (Confidential).

component was identified as 3-fluoro-3-(difluoramino)hexane.* When water was added to the pentane-insoluble material, another product separated, which was identified as N-(1-difluoraminopropyl)propionamide.

The most likely mechanism for the formation of 3-fluoro-3-(difluoramino)haxane is the addition of hydrogen fluoride to 3-hexyne to form 3-fluoro-3-hexene followed by the addition of difluoramine. This course was confirmed, in a separate experiment, by bubbling anhydrous hydrogen fluoride into a refluxing mixture of 3-hexyne and difluoramine to give the same compound.

The source of the 3,3-bis(difluoramino)hexane in this reaction does not appear to be the reaction of the ketone with difluoramine, since one experiment using 3-pentanone in the presence of $BF_3 \cdot H_3PO_4$ failed to give the gem-difluoramine. It appears possible that the gem-difluoramine was formed from 3-fluoro-3-(difluoramino)hexane.

The formation of N-(1-difluoraminopropyl)propionamide may be explained by the addition of difluoramine to the triple bond to form a vinyl difluoramine. However, rather than rearrange to an α-fluoro-fluorimine, as happens in the addition of tetrafluorohydrazine to acetylenes,** the vinyl difluoramine could lose a fluoride ion to form a fluoriminocarbonium ion, which can be trapped by difluoramine. The Beckmann rearrangement of the resulting fluorimine would give the amide. The other possible Beckmann rearrangement product, $CH_3CH_2CH(NF_2)\overset{\overset{O}{\|}}{C}NHCH_2CH_3$, resulting from ethyl migration, was not found. It would be expected to be hydrolytically unstable.

The reactions of difluoramine with 3-hexyne catalyzed by $BF_3 \cdot H_3PO_4$ are summarized in the following equations:

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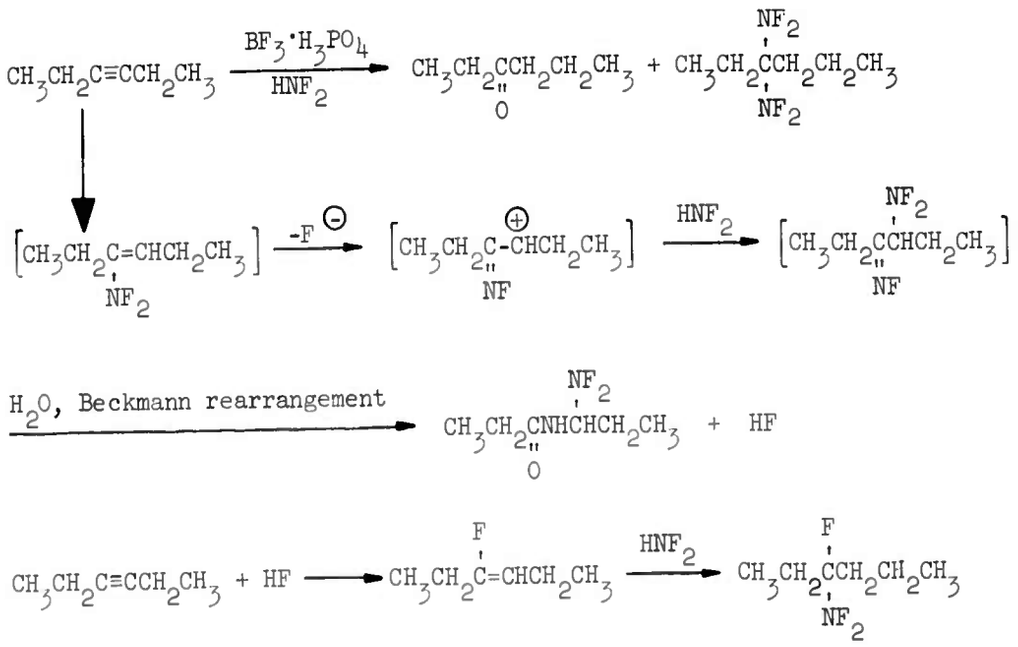
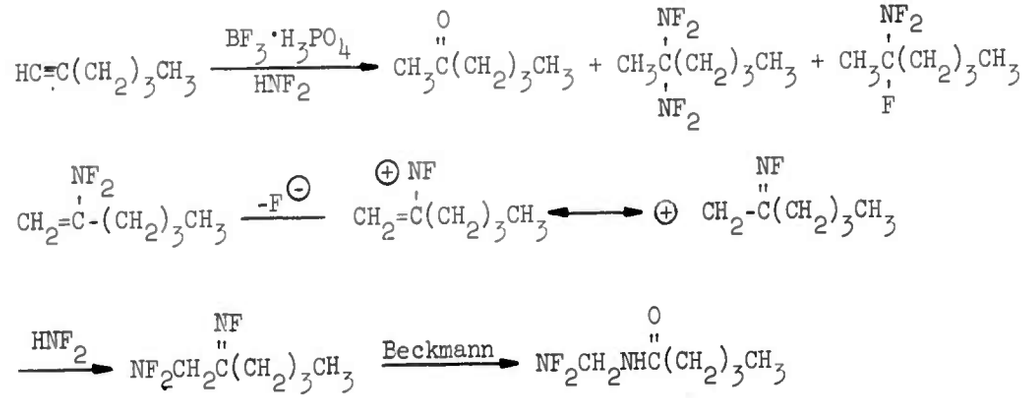
*Aerojet-General Report 0235-01-15, January 1963, p. 4 (Confidential).
Aerojet-General Report 0235-01-16, March 1963, p. 3 (Confidential).

**Rohm & Haas Co., Report P-59-18, 21 October 1959, p. 12 (Confidential).



Similar reactions were observed when 1-hexyne was used as the starting material; 2-hexanone, 2,2-bis(difluoramino)hexane, 2-fluoro-2-(difluoramino)-hexane, 2-fluoro-2-(difluoramino)hexane and N-(difluoraminomethyl)-valeramide were formed:



b. Reaction of Haloolefins with Difluoramine

There are indications discussed above, that the formation of a gem-difluoramine from an acetylene and difluoramine in the presence of $BF_3 \cdot H_3PO_4$ takes place through an intermediate α-fluorodifluoraminoalkane. The possibility that difluoramino groups facilitate solvolysis reactions of this type was investigated further, since the method could lead to new classes of NF compounds.

When vinylidene chloride was treated with refluxing difluoramine and $BF_3 \cdot H_3PO_4$, no reaction occurred, and starting material was recovered. The use of a pressure tube for this reaction resulted in an explosion. Subsequently, 20% fuming sulfuric acid was used as the catalyst in a pressure reaction which ran for 18 hours at ambient temperature. The product, isolated by extracting the mixture with pentane after the excess difluoramine was removed, consisted of two compounds. These were isolated by gas chromatography. The compound with the longer retention time was identified by its infrared spectrum (Figure 1), its proton (Figure 2) and fluorine (Figure 3) NMR spectra and elemental analysis as 1,1-dichloro-1-(difluoramino)ethane. The other compound was found from its infrared spectrum (Figure 4), proton (Figure 5) and fluorine (Figure 6) NMR spectra and elemental analysis to be 1-chloro-1,1-bis(difluoramino)ethane.

$$Cl_2C{=}CH_2 \xrightarrow[H_2SO_4,\ SO_3]{HNF_2} NF_2Cl_2CCH_3 \ + \ (NF_2)_2CClCH_3$$

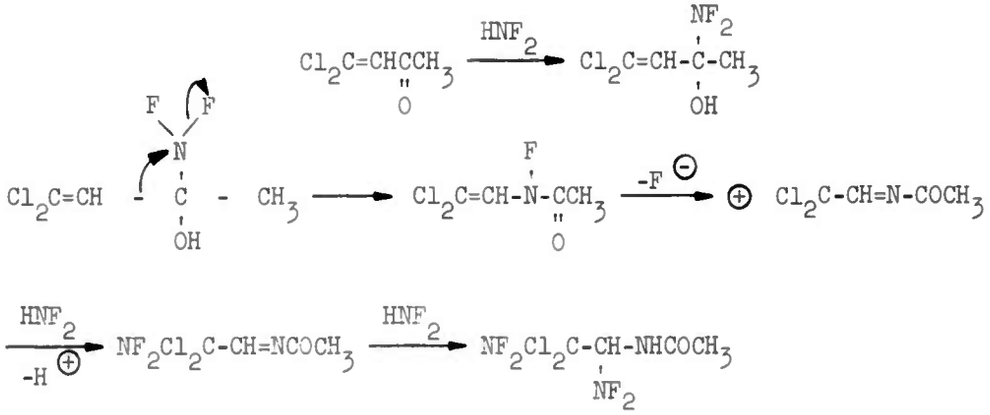
The reaction was repeated in an attempt to replace the remaining chlorine, using 30% fuming sulfuric acid as the catalyst. A material was isolated which showed only a septet in its proton NMR spectrum, as would be expected for 1,1,1-tris(difluoramino)ethane. The nitrogen analysis was 19.5% (calc'd for 1,1,1-tris(difluoramino)ethane: 22.9%, for 1-chloro-1,1-bis(difluoramino)ethane: 16.8%). The material decomposed, however, before complete analytical data could be obtained. The preparation is being repeated.

The reaction of 1,1-dichloro-1-buten-3-one with difluoramine was expected, by analogy to the reaction of the unchlorinated substrate* to result in a rapid Michael addition followed by the replacement of the carbonyl, and possibly the chlorines. When this material was treated with a large excess of refluxing difluoramine in 20% fuming sulfuric acid, a 57% yield of 1,1-dichloro-3,3-bis(difluoramino)-1-butene was obtained. Thus, the chlorines inhibited Michael addition. The infrared spectrum of the product is shown in Figure 7 and the proton and fluorine NMR spectra are given in Figures 8 and 9.

*Aerojet-General Report 0235-01-11, 14 July 1961, p. 2 (Confidential).

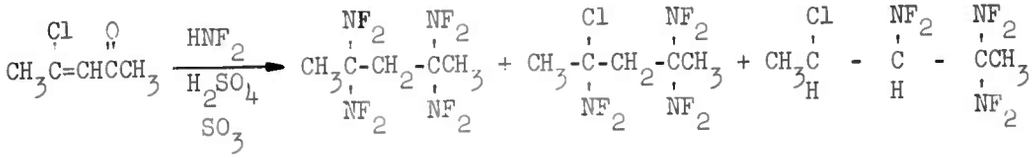
When this reaction was repeated, using seven times the amount of ketone with the same amount of difluoramine, this product was not isolated. Instead, a white crystalline solid was formed which was identified as N-[2,2-dichloro-1,2-bis(difluoramino)ethyl]acetamide. The white solid's infrared spectrum and proton and fluorine NMR spectra are given in Figures 10, 11, and 12, respectively. The structure was further confirmed by exchanging the amide hydrogen with D_2O and obtaining the proton NMR spectrum of the deuterated material to eliminate NH coupling. This NMR spectrum is shown in Figure 13.

This product could be formed by the Beckmann rearrangement of the initial difluoramine adduct, 1,1-dichloro-3-difluoramino-1-buten-3-ol to give N-2,2-dichlorovinyl-N-fluoroacetamide. The ionization of this "allylic" NF and the reaction of the resulting carbonium ion with difluoramine would give 1,1-dichloro-1-difluoramino-2-N-acetyliminoethane. The addition of difluoramine would then give N-[2,2-dichloro-1,2-bis(difluoramino)ethyl]acetamide.



Attempts to react acetylacetone with difluoramine had been unsuccessful. The addition of difluoramine to 2-chloro-2-penten-4-one was examined as a method of preparing 2,2,4,4-tetrakis(difluoramino)pentane. The desired product was obtained in 90% purity when this reaction was carried out at ambient temperature, under autogenous pressure, in the presence of 20% fuming sulfuric acid. The infrared, proton, and fluorine NMR spectra of 2,2,4,4-tetrakis(difluoramino)pentane, purified by gas chromatography, are given in Figures 14, 15, and 16, respectively. Two compounds, each comprising approximately 5% of the sample, were also isolated by gas chromatography and were characterized as

2-chloro-2,4,4-tris(difluoramino)pentane and 2-chloro-3,4,4-tris(difluoramino)-pentane. The infrared and proton and fluorine NMR spectra of the former are shown in Figures 17, 18, and 19, and those of the latter, in Figures 20, 21, and 22, respectively.



The preparation of 2,2,4,4-tetrakis(difluoramino)pentane directly from acetylacetone was reported recently.*

An attempt to react chloroprene with difluoramine in the presence of $BF_3 \cdot H_3PO_4$ gave a polymeric material. An attempted reaction of ethyl 3-chlorocrotonate with refluxing difluoramine in 20% fuming sulfuric acid resulted only in the recovery of starting material.

c. Reactions of gem-Difluoramines

The previously begun study of reactions of model NF compounds** was continued with the object of determining whether various commonly used organic synthesis procedures may be applied without interference by the NF groups.

The study of reactions of gem-difluoramines, using 2,2-bis(difluoramino)-octane as a model was continued.*** Several reducing agents were treated with 2,2-bis(difluoramino)octane in order to find experimental conditions which might be used to reduce a functional group such as carbonyl or carboxyl without attacking the NF bonds. One such reagent was lithium borohydride in ether, from which 81% of the starting material was recovered after 20 hours at ambient temperature. Esters can be reduced under these conditions.****

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*Rohm & Haas Co. Quarterly Progress Report on Process Research, Report No. P-63-9, June 17, 1963, p. 10 (Confidential).

**Aerojet-General Report 2381, October 1962, p. 40 (Confidential).

***Aerojet-General Report 0235-01-15, January 1963, p. 1 (Confidential).

****Sodium Borohydride and Potassium Borohydride, Metal Hydrides Inc., 1958.

Lithium aluminum hydride also appears to be applicable in the presence of NF groups. The reaction of 2,2-bis(difluoramino)octane with lithium aluminum hydride in ether at ambient temperature for 1 hour resulted in the recovery of 80% of the unreacted starting material.

The 2,2-bis(difluoramino)octane was also recovered in high yield when it was treated with methanolic hydrazine at ambient temperature for 20 hours. The preparation hydrazides containing gem-difluoramino group should therefore be practical.

The exploration of the limits of stability of gem-difluoramines toward basic reagents was carried further by treating 2,2-bis(difluoramino) octane with sodamide in liquid ammonia. The reaction was quenched approximately 20 min after the addition of the NF compound to sodamide in refluxing ammonia was completed, and 45% of the starting material was recovered. No other product was isolated from the tarry distillation residue.

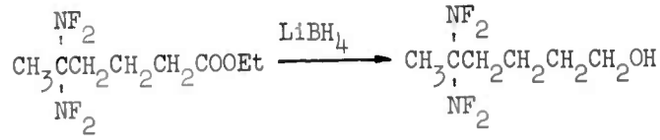
Butyl lithium in hexane reacted vigorously and instantaneously with 2,2-bis(difluoramino)octane; no starting material was recovered. Some n-octane was isolated, as well as an unidentified high-boiling liquid which contained only C, H and N. When the reaction was repeated using 2,2-bis(difluoramino) propane, a material with similar infrared absorption was obtained, but again the elemental analysis could not be assigned to a definite structure. The isolation of n-octane in these reactions suggests an attack on fluorine to give n-butyl fluoride which then undergoes a Wurtz reaction.

The stability of 2,2-bis(difluoramino)octane toward boron trifluoride and nitric acid was also examined. The starting material was recovered quantitatively after gaseous BF_3 was bubbled through it for 2 hours. The reaction with concentrated nitric acid at 95°C for 30 min resulted in a 75% recovery of starting material.

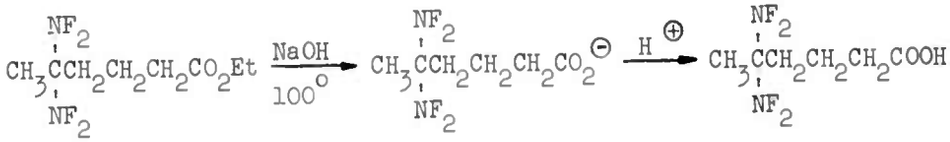
Some reactions of ethyl 5,5-bis(difluoramino)hexanoate were also studied in order to show the effect of gem-difluoramines on carboxyl group reactions. This compound was previously prepared by the reaction of ethyl

5-ketohexanoate with difluoramine in concentrated sulfuric acid.* The yield of this preparation has been increased to 83% by substituting 20% fuming sulfuric acid for the concentrated reagent and reducing the reaction time.**

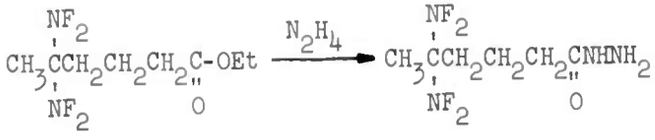
When this ester was treated with lithium borohydride in tetrahydrofuran for 1 day, it was converted in 49% yield to 5,5-bis(difluoramino)-1-hexanol.**

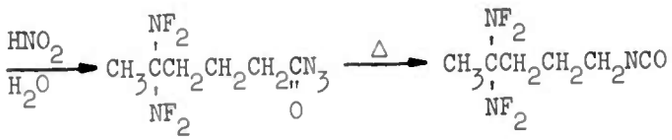


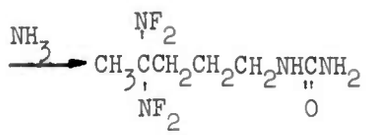
The hydrolysis of ethyl 5,5-bis(difluoramino)hexanoate was accomplished with refluxing aqueous 10% sodium hydroxide. The starting material, which was water insoluble, was gradually consumed over a 1-1/2 hr period. Acidification then gave a 79% yield of 5,5-bis(difluoramino)hexanoic acid.



Another reaction of ethyl 5,5-bis(difluoramino)hexanoate which was investigated was its conversion to the corresponding isocyanate by the Curtius reaction.***







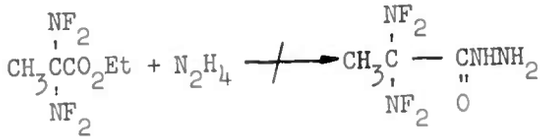
*Aerojet-General Report 0235-01-14, June 1962, p. 9 (Confidential).

**Aerojet-General Report 0235-01-15, January 1963, p. 3 (Confidential).

***Aerojet-General Report 0235-01-16, March 1963, p. 6 (Confidential).

The hydrazide, prepared by heating the ester with methanolic hydrazine, was not characterized, but was treated directly with nitrous acid. Decomposition of this azide in chloroform gave a product which was indicated by its infrared spectrum to be a mixture containing approximately equal amounts of the original ester and the isocyanate. Evidently the preparation of the hydrazide was incomplete. The isocyanate was characterized by converting it to the corresponding urea, a solid derivative, by the addition of gaseous ammonia.

The extension of this reaction series to ethyl 2,2-bis(difluoramino)propionate, which was recently prepared,* was attempted.** However, several attempts to prepare the hydrazide were unsuccessful, and inorganic fluorides were formed. The results are similar to those reported by Rohm & Haas*** for the reaction of ammonia with ethyl 2,2-bis(difluoramino) propionate.



The reaction of this ester with lithium borohydride, under the conditions that were used to reduce ethyl 5,5-bis(difluoramino)hexanoate, gave no new NF compounds.

A brief study was also made of some reactions of 1,3,3-tris(difluoramino)-butane, which was prepared by the reaction of methyl vinyl ketone with difluoramine in sulfuric acid.**** The yield of this adduct was increased to 60% by using a large excess difluoramine, with 100% sulfuric acid as the dehydrating agent. The reaction of 1,3,3-tris(difluoramino)butane with lithium borohydride in tetrahydrofuran gave 1-amino-3,3-bis(difluoramino)butane, isolated as the hydrochloride.*****

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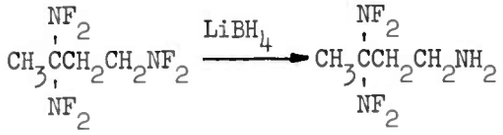
*Rohm & Haas, Quarterly Progress Report on ARPA Projects, No. P-62-26, p. 5 (Confidential).

**Aerojet-General Report 0235-01-17, June 1963, p. 5 (Confidential).

***Rohm & Haas, QPR on ARPA Projects, No. P-62-26, p. 5 (Confidential).

****Aerojet-General Report No. 0235-01-11, July 1961, p. 8 (Confidential).

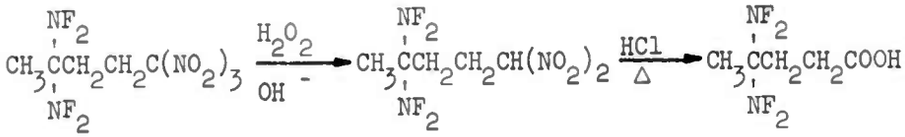
*****Aerojet-General Report No. 0235-01-16, March 1963, p. 5 (Confidential).



Some unsuccessful attempts were made to dehydrofluorinate 1,3,3-tris(difluoramino)butane to 3,3-bis(difluoramino)butyronitrile. The reaction with sodium methoxide in methanol for 1/2 hour at room temperature resulted in the recovery of only 36% of the starting material, but no other product was found. No reaction took place when gaseous ammonia was bubbled through a pentane solution of the tris(difluoramino)butane.

An investigation was also begun of the synthetic usefulness of 5,5,5-trinitro-2,2-bis(difluoramino)pentane, which was prepared by the reaction of the corresponding ketone with difluoramine.* Attempts to prepare γ,γ-bis(difluoramino)carboxylic acids from the corresponding ketoacids have been unsuccessful. Another potential route to these structures is the hydrolysis of the appropriate trinitromethyl compounds. Kamlet, Kaplan, and Dacons have reported that some electronegatively substituted trinitromethyl compounds could be hydrolyzed to carboxylic acids with refluxing hydrochloric acid.** However, when this method was applied to 5,5,5-trinitro-2,2-bis(difluoramino)pentane, no reaction took place and the starting material was recovered.***

Since terminal dinitro compounds are hydrolyzed more easily than are unactivated trinitromethyl compounds,** 5,5-dinitro-2,2-bis(difluoramino)pentane was synthesized by treating the trinitro compound with alkaline hydrogen peroxide.****



*Aerojet-General Report No. 0235-01-13, March 1962, p. 9 (Confidential).

**M. J. Kamlet, L. A. Kaplan and J. C. Dacons, J. Org. Chem., 26, 4371 (1961).

***Aerojet-General Report No. 0235-01-16, March 1963, p. 7 (Confidential).

****Aerojet-General Report No. 0235-01-17, June 1963, p. 1 (Confidential).

The dinitro compound was heated with constant boiling hydrochloric acid for 4 hours to form 4,4-bis(difluoramino)pentanoic acid. The product was contamined with some starting material, which could not be separated by distillation. The pure acid was obtained, however, by treating the mixture with sodium hypochlorite to convert the dinitro compound to 5-chloro-5,5-dinitro-2,2-bis(difluoramino)-pentane, which was extracted from the alkaline solution. Acidification, extraction, and distillation then gave the pure acid, the infrared spectrum of which is shown in Figure 23.

The preparation of the starting material, 5,5,5-trinitro-2,2-bis(difluoramino)-pentane, was found to be very sensitive to experimental conditions. The use of a large excess of 100% sulfuric acid as the solvent for the reaction of difluoramine with 5,5,5-trinitro-2-pentanone required a pressure reactor and a 40-hour reaction period.* Even then, a considerable amount of starting material was recovered. When a relatively small amount of 20% fuming sulfuric acid was used as the solvent, the reaction was complete after 2 hours at the reflux temperature of difluoramine, and a quantitative yield was obtained.**

The ionization constant of 4,4-dinitropentanoic acid has been reported.*** Since the analogous difluoramino compound and the next higher homologue have become available, the ionization constants of these acids were determined. The values give an indication of the electronegativity of a geminal bis-difluoramino group as compared to a geminal dinitro group. The pK_a reported by NOL for 4,4-dinitro-pentanoic acid was 4.0 $\pm$ 0.1 at 25°C in dilute aqueous solution. Under similar conditions the pK_a of 4,4-bis(difluoramino)pentanoic acid was found to be 4.24 $\pm$ 0.1, while that of 5,5-bis(difluoramino)hexanoic acid was 4.68 $\pm$ 0.1.

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* Aerojet-General Report 0235-01-13, March 1962, p. 9 (Confidential).

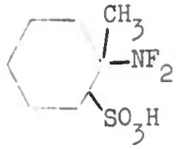
** Aerojet-General Report 0235-01-17, June 1963, p. 2 (Confidential).

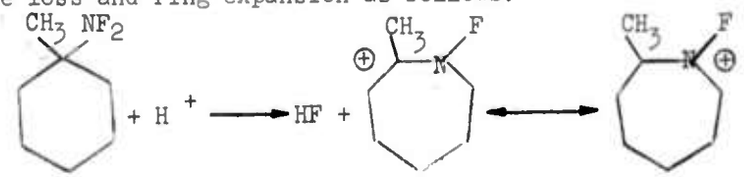
*** U.S. Naval Ordnance Laboratory, Navord Report 2809, "The Acid Strength of Aliphatic Nitro Compounds," 11 March 1953, p. 3 (Confidential).

d. Reactions of Alkyldifluoramines

It was previously found that t-butyl difluoramine reacted with sulfuric acid to form a soluble intermediate which gave acetone on dilution with water.* It was postulated that the intermediate was the sulfonation product, which might be hydrolyzed to methanesulfonic acid and acetone. Since methanesulfonic acid cannot be separated easily from sulfuric acid, 1-methyl-1-(difluoramino)cyclohexane was used as the starting material in the hope of obtaining a product with both degradation fragments tied into the same molecule. 1-Methyl-1-(difluoramino)cyclohexane was synthesized in 83% yield by the reaction of 1-methyl-1-cyclohexene with difluoramine in the presence of $BF_3 \cdot H_3PO_4$.**

This compound was found to react exothermically with concentrated sulfuric acid, giving a colorless, homogeneous solution. However, when an attempt was made to distill the product which was isolated after quenching, the product decomposed.

The F^{19} NMR spectrum of a freshly prepared solution of 1-methyl-1-(difluoramino)cyclohexane in sulfuric acid consisted of a poorly resolved triplet at -4104 cps (J = 16 cps) relative to external $CFCl_3$, and a singlet at -2159 shown to be due to HF. The triplet cannot be attributed to the expected sulfonic acid  . The results, however, can be explained by fluoride loss and ring expansion as follows:

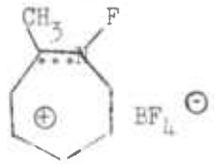


An attempt was made to isolate a salt containing this novel ion by passing gaseous boron trifluoride into a solution of 1-methyl-1-(difluoramino)cyclohexane in sulfur dioxide. Evaporation of the SO_2 left a liquid which still had a slight odor of SO_2. The F^{19} spectrum contained a

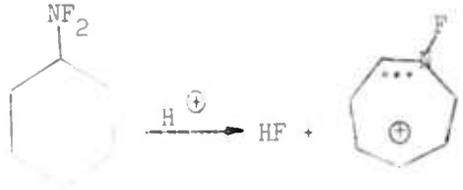
*Aerojet-General Report 2099, November 1961, p. 10 (Confidential).
Aerojet-General Report 0235-01-13, March 1962, p. 4 (Confidential).

**Aerojet-General Report 0235-01-16, March 1963, p. 4 (Confidential).

triplet at -3922 (J = 17 cps), and a singlet at +8524, attributable to BF_4^-. When pentane, rather than SO_2, was used as the solvent in this preparation, a hygroscopic solid was isolated which was found by elemental analysis to be



Since secondary alkyl difluoramines are also known to be unstable to strong acids,* it was of interest to examine the structure of the decomposition products. When a sample of difluoraminocyclohexane was shaken with sulfuric acid, it reacted exothermically to give a clear solution. The NMR spectra of this sulfuric acid solution** showed the presence of HF and the ring-expanded cation analogous to that from 1-methyl-1-difluoraminocyclohexane.



This type of rearrangement may be the cause of the general instability of non-geminal NF_2 groups toward strongly ionizing acids. The stabilizing effect of adjacent NF_2 groups may be attributed to the inductive effect, which would increase the energy of the resulting ion.

The reduction of these cycloalkyl difluoramines with lithium aluminum hydride was also studied.*** The reduction product of 1-methyl-1-(difluoramino)cyclohexane was found to be a mixture of amines with the empirical formula $C_7H_{15}N$. The Hinsberg test of this mixture gave no acid-soluble or base-soluble products, indicating a mixture of secondary amines. The NMR spectrum of the mixture of benzenesulfonamides contained signals identical to those of an authentic sample of the benzenesulfonamide of N-methyl-cyclohexylamine. In addition, there were signals assignable to the derivative of 2-methylhexamethyleneimine. There was also a second methyl peak, possibly due to the benzenesulfonamide

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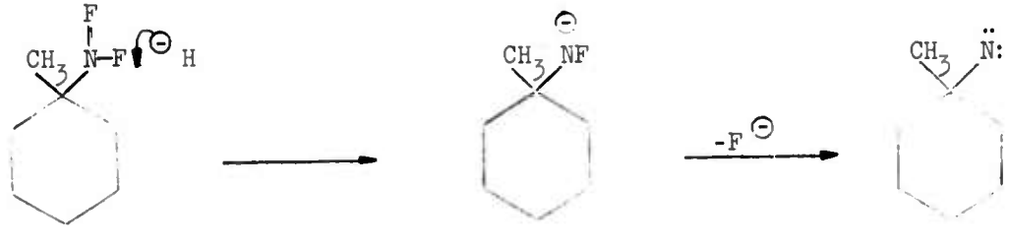
*Aerojet-General Report 0235-01-17, June 1963, p. 4 (Confidential).

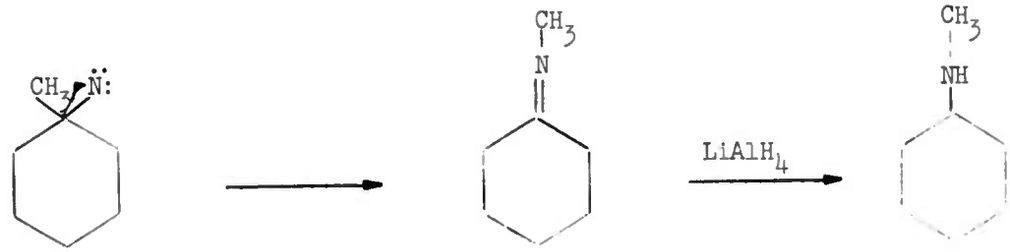
**Aerojet-General Report 2381, October 1062, p. 11 (Confidential).

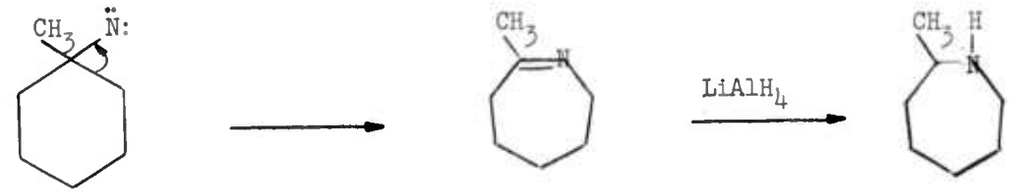
***Aerojet-General Report 0235-01-17, June 1963, p. 2 (Confidential).

of 1-methyl-1-cyclohexylamine (this hindered sulfonamide might have unusual solubility properties). Attempts to resolve the mixture of amines by gas chromatography were unsuccessful.

The rearranged amines might be formed from the nitrene resulting from hydride attack on fluorine followed by loss of fluoride.







The reduction of difluoraminocyclohexane with lithium aluminum hydride followed a similar course. The product was a 70:30 mixture of hexamethylenimine and cyclohexylamine. It was identified by comparing the NMR spectra and gas-chromatograph retention times with those of authentic samples.

Similar rearrangements have been reported in the reduction of cyclic nitro compounds.*

2. Experimental

a. Reaction of 1,1-Dichloroethylene with Difluoramine

1,1-Dichloroethylene (3 g, 0.031 moles) was added to a refluxing mixture of approximately 27 g of difluoramine and 10 ml of 20% fuming sulfuric acid in a 500-cc pressure reactor. The mixture was cooled with dry ice and the pressure valves were closed. An insoluble upper layer formed after the mixture had reacted at room temperature for 2 hours. The reactor was again cooled with dry ice and the pressure valves were opened for 10 min to release low-boiling gasses. The mixture was then allowed to react at room temperature for 18 hours. The reactor was then vented and 50 ml of pentane was added. The layers were separated and the pentane solution was distilled through a 25-cm platinum spiral column to give 0.51 g of product, b.p. 30°C/160 mm. Gas chromatography was carried out using a 10-ft by 1/4-in. column of 10% dioctyl phthalate on Teflon at room temperature with a helium flow rate of 60 cc/min. Two components with retention times of 18 min and 27 min (relative areas of 1:2) were trapped and identified as 1-chloro-1,1-bis(difluoramino)ethane and 1,1-cichloro-1-(difluoroamino)ethane, respectively. Due to volatility losses, there was not enough of the former material for a complete analysis.

Anal. Calcd. for $C_2H_3N_2F_4Cl$: N, 16.8. Found: N, 17.3.

The 60-mc proton spectrum (Figure 5) was obtained using a CCl_4 solution with TMS added as an internal reference and employing the Varian microcell. The spectrum consists of a single signal, a quintet with a splitting of a few cycles per second, at 1.61 ppm. The 56.4 mc F^{19} NMR spectrum (Figure 6)

*G. E. Lee, et. al., Chem. and Ind., 1958, 417.

was obtained by using the same sample, with $CFCl_3$ added as an internal reference. The spectrum consists of a single, relatively broad signal at -160 ± 3 cps (-27.7 ppm). Complete analytical data was obtained for 1,1-dichloro-1-(difluoramino)-ethane.

Anal. Calcd. for $C_3H_3Cl_2NF_2$: C, 16.0; H, 2.0; N, 9.34; F, 25.3. Found: C, 15.8; H, 2.26; N, 8.91; F, 25.3.

The proton NMR spectrum (Figure 2) consists of a triplet with a splitting of a few cps at 2.31 ppm. The fluorine spectrum (Figure 3) consists of a single, relatively broad signal at -2449 ± 4 cps (-43.4 ppm).

This synthesis was repeated using 30% fuming sulfuric acid as the catalyst. n-Decane was used as the extraction solvent to avoid the loss of volatile product which probably resulted during the distillation of pentane in the previous run. The product was pumped directly from this n-decane solution into the gas loop of the gas chromatograph. The same peaks, with retention times of 18 min and 27 min were obtained but with equal areas. The partial analysis of the first peak indicated a new material, as described in the Discussion, but characterization is still in progress.

b. 1,1-Dichloro-3,3-bis(difluoramino)-1-butene

Approximately 27 g of difluoramine was refluxed over 10 ml of 20% fuming sulfuric acid, and 3 g (0.028 moles) of methyl dichlorovinyl ketone* was added dropwise. The mixture was allowed to reflux for 3 hours. Pentane (50 ml) was then added and the unreacted difluoramine was allowed to escape. The layers were separated and the pentane solution was dried over sodium sulfate. The solvent was distilled off through a 25-cm platinum spiral column. The residue was vacuum-distilled to give 3.64 g (0.016 moles, 57% yield) of 1,1-dichloro-3,3-bis(difluoramino)-1-butene, b.p. 51°C/18 mm.

Anal. Calcd. for $C_4H_4N_2F_4Cl_2$: C, 21.1; H, 1.76; N, 12.3; F, 33.5. Found: C, 20.9; H, 2.04; N, 12.2; F, 34.1.

The 60-mc proton NMR spectrum (Figure 8) was obtained using a CCl_4 solution with TMS added as an internal reference and the 56.4 mc F^{19}

*I. M. Heilbow, E. R. H. Jones, and M. Julia, J. Chem. Soc., 1949, 1430.

NMR spectrum (Figure 9) was obtained using the same solution with $CFCl_3$ added as an internal reference. A Varian microcell was employed. The proton spectrum consists of a quintet at 1.97 ppm and a somewhat broadened singlet at 6.31 ppm. The quintet indicates the partial structure $CH_3C(NF_2)_2-$. The chemical shift of the other signal indicates that it is assignable to an olefinic proton. The spectrum can be rationalized on the basis of the structure $CH_3C(NF_2)_2CH = CCl_2$. The quintet is assigned to the methyl group and the 6.31 ppm signal to the olefinic proton. The F^{19} NMR spectrum consists of a single signal at -1693 cps (-30.02 ppm).

c. N-[2,2-Dichloro-1,2-bis(difluoramino)ethyl]acetamide

Methyl dichlorovinyl ketone (20 g, 0.144 moles) was added dropwise to a refluxing mixture of 27 g of difluoramine and 65 ml of 20% fuming sulfuric acid. The solution was allowed to reflux for 3 hours, then 60 ml of pentane was added and the unreacted difluoramine was vented off. The acid layer was drained into a beaker containing 100 g of ice. The aqueous layer was extracted with three 30 ml portions of methylene chloride which were combined and dried over sodium sulfate. The pentane layer was distilled through a 25-cm platinum spiral column, but no products were found. The methylene chloride solution was distilled off and 14.6 g of yellow oil remained. The oil was dissolved in hot cyclohexane. White crystals formed upon cooling the solution to room temperature. The solid was recrystallized and dried in vacuum to give 8.8 g (0.0341 moles, 23.7% yield) of N-[2,2-dichloro-1,2-bis(difluoramino)ethyl]acetamide, m.p. 92-93°C.

Anal. Calcd. for $C_4H_5N_3F_4OCl_2$: C, 18.6; H, 1.94; N, 16.3; F, 29.4; Cl, 27.6. Found: C, 19.4; H, 2.04; N, 16.2; F, 28.4; Cl, 32.9.

The 60-mc proton (Figure 11) and 56.4-mc F^{19} (Figure 12) NMR spectra were obtained using a solution in $CDCl_3$ with TMS and $CFCl_3$ as an internal reference. The F^{19} spectrum consists of two multiplets, a doublet (splitting 23 cps) at -42.66 ppm, and a "Nonequivalence" quartet (chemical shifts -27.37 and -45.34 ppm, J = 614 cps). The members of the nonequivalence quartet are further split into doublets (low field splitting 11.4 $\pm$ 0.2 cps, high field

splitting 22.3 ± 0.2 cps). The quartet is readily assignable to the -CH(NF_2)- difluoramino group. The fluorines are rendered nonequivalent by virtue of the attachment of the group to an asymmetric carbon and the doublet splittings are produced by coupling to the proton on the carbon. The doublet is then assigned to the -C(NF_2)Cl_2-difluoramino group. The 23-cps splitting is too large to result from coupling to the proton on the adjacent carbon and must result from a nonequivalence of the two fluorines. This could possibly result from rotational isomerism or conceivably from hydrogen-bonding to one of the fluorines.

The proton spectrum consists of an intense singlet at 2.19 ppm (assigned to the acetyl methyl $\underline{CH_3}CO$-), a broadened poorly resolved [splitting approximately 9 cps, assigned to the amide proton -CON$\underline{H}$CH(NF_2)-], and a group of five signals centered on 6.19 ppm (which is assigned to the -NHC$\underline{H}$(NF_2)- proton). The form of the signal arises in the following way. The signal is split twice into doublets (22.9 cps and 11.3 ± 0.4 cps) by the nonequivalent -NF_2 fluorines, and again into doublets by coupling to the amide proton. The N$\underline{H}$C$\underline{H}$ coupling constant is nearly equal to one of the H-F coupling constants so that the four resulting doublets overlap to produce five evenly spaced signals.

The sample was treated with D_2O to remove exchangeable protons (Figure 13). The 6.86 ppm doublet disappears confirming its assignment to the amide proton and the 6.19 ppm signal reverts to the pair of doublets expected for coupling to two nonequivalent fluorines. The 2.19 ppm $\underline{CH_3}CO$- signal is unaffected.

d. Reaction of 2-Chloro-2-pentene-4-one with Difluoramine

2-Chloro-2-pentene-4-one* (3 g, 0.028 moles) was added to a refluxing mixture of approximately 18 g of difluoramine and 10 ml of 20% fuming sulfuric acid in a 200 cc pressure reactor. The mixture was cooled with dry ice and the pressure valves were closed. The mixture was allowed to react at room temperature for 20 hours. An insoluble upper layer formed during this time. The reactor was vented and 50 ml of pentane was added. The layers were separated and the pentane solution was distilled through a 25 cm platinum spiral column to give 0.42 g of product, bp 30°C, 1 mm.

*M. Julia, Ann. Chim. [12], 5, 595 (1950).

Gas chromatography, using an 8-ft by 1/4-in. column of 10% dioctyl phthalate on Teflon at 95° with a helium flow of 75 cc/min gave three peaks with retention times of 56, 66, and 81 min and relative areas of 90%, 5% and 5%, respectively. The major peak was identified as 2,2,4,4-tetrakis-(difluoramino)pentane.

Anal. Calcd. for $C_5H_8N_2F_4$: C, 21.8; H, 2.90; N, 20.3; F, 55.1. Found: C, 21.8; H, 3.20; N, 20.0; F, 50.9.

The proton NMR spectrum (Figure 15) was taken in CCl_4 with TMS as an internal standard in a Varian microcell. It consists of a poorly resolved quintet at 1.77 ppm and a broadened, unresolved signal at 2.90 ppm. The quintet is assigned to the terminal methyl groups in the tetrakis compound, $\underline{CH_3}C(NF_2)_2CH_2C(NF_2)_2\underline{CH_3}$. The signal at 2.90 ppm is assigned to the internal methylene group. The F^{19} spectrum (Figure 16) of the same sample with $CFCl_3$ added consists of a single, relatively narrow signal at -1593 cps (028.24 ppm). It is assigned to the difluoramino groups.

The two minor components were found to be isomeric tris-(difluoramino)chloropentanes.

Anal. Calcd. for $C_5H_8ClN_3F_6$: C, 23.1; H, 3.09; N, 16.2; F, 44.0. Found for the material with a 66-min retention time: C, 23.5; H, 3.34; N, 15.9; F, 42.9. Found for the material with 81-min retention time: C, 23.6; H, 3.28; N, 15.7; F, 43.7.

The former compound was assigned the structure, 2-chloro-2,4,4-tris(difluoramino)ethane, on the basis of its NMR spectra. The proton spectrum in CCl_4 with a TMS internal standard (Figure 18) consists of a quintet at 1.79 ppm, a poorly resolved triplet at 1.97 ppm and a broadened, unresolved signal at 2.93 ppm. The quintet is assigned to the $CH_3C(NF_2)_2$-methyl group, the triplet to the $-CC(NF_2)CH_3$ methyl group and the signal at 2.93 ppm to the internal methylene group. The F^{19} spectrum with a $CFCl_3$ internal standard (Figure 19) consists of three broadened signals at -1508 cps (-26.7 ppm), -1641 cps (-29.1 ppm) and -1976 cps (-35.0 ppm). On the basis of the structure indicated by the

proton spectrum two multiplets would be expected; a slightly broadened, unresolved signal for the gem-difluoramino groups $CH_3C(NF_2)_2$- and a "nonequivalence" quartet for the $-CCl(NF_2)CH_3$ difluoramino group. Thus, one of the signals may be assigned to the gem-difluoramino groups, and the two others regarded as the central members of the quartet. The outer members may well be too weak to observe. There seems to be no clearcut choice for the assignment. The two central members of the quartet should be relatively weak and the gem-difluoramino signal relatively strong, but all of the signals are of about the same strength. The fluorine spectrum is thus somewhat ambiguous.

The proton (Figure 21) and fluorine (Figure 22) NMR spectra of the latter compound can be rationalized on the basis of the structure, 2-chloro-3,4,4-tris(difluoramino)pentane.

The assignments are as follows:

The quintet at 1.91 ppm is assigned to the $-C(NF_2)_2\underline{CH_3}$ methyl group. The multiplet to high field of the quintet is reinterpreted as a pair of doublets (splitting approximately 6.3 cps) at 1.58 and 1.62 ppm which are assigned to the $\underline{CH_3}CHCl$-methyl group in two diastereo-isomers. (It will be noted that the structure indicated has two centers of asymmetry.) The signal with maximum intensity at 273 cps is assigned to the $CH_3\underline{CH}Cl$- proton. This proton would be coupled to those of the methyl group, the proton on the adjacent carbon, and the fluorines of the NF_2 group on the adjacent carbon. The expected form of the signal is difficult to predict, but the poorly resolved multiplet observed is not unreasonable. The broad, weak, complicated multiplet to the high field of the 273 cps signal is then assigned to the $-\underline{CH}(NF_2)$- proton. This signal would be split into a pair of doublets (10-20 cps) by the nonequivalent NF_2 fluorines, again into doublets by the proton on the adjacetn carbon (5-10 cps) and further into quintets (2-3 cps) by the gem-NF_2 groups on the other adjacent carbon. Thus, the complexity of the signal is to be expected.

The F^{19} signal at -1599 cps (-28.4 ppm) is assigned to the gem-NF_2 groups, $-C(NF_2)CH_3$. No other signals of comparable intensity are

evident but this fact can be rationalized in the following way. The $-CH(NF_2)-$ signal intensity would be divided between two diastereo-isomers. Each of these signals would appear as a nonequivalence quartet since the point of attachment is asymmetric. The components of the quartets would be further split into doublets by coupling to the proton on the same carbon. Thus half the intensity of the -1599 cps would be distributed among 16 multiplet components. In addition the multiplet may be partially overlapped by the -1599 cps signal. Thus it is perhaps not surprising that no other signals of appreciable intensity are observed.

e. Reaction of Ethyl 3-Chlorocrotonate with Difluoramine

Ethyl 3-chlorocrotonate (3 g, 0.02 moles) was added to a refluxing mixture of approximately 27 g of difluoramine and 10 ml of 20% fuming sulfuric acid. A yellow upper layer was observed. The mixture was allowed to reflux for 3 hours then 50 ml of pentane was added and the unreacted difluormine allowed to escape. The acid layer was quenched in ice water then extracted with methylene chloride and dried over sodium sulfate. No products were found in the methylene chloride. The pentane solution was distilled to give 2.1 g of starting material only.

f. Reaction of Chloroprene with Difluoramine

Approximately 27 g of difluoramine was refluxed over 5 g (0.062 moles) of freshly distilled chloroprene and 1 ml of boron trifluoridephosphoric acid complex was added. An insoluble upper layer formed after the mixture had reacted at room temperature for 3 hours. Pentane (50 ml) was added and the unreacted difluoramine was allowed to escape. The catalyst was separated and the pentane solution was [illegible] over sodium sulfate, and distilled off through a 25-cm platinum [illegible] umn. The residue (3.6 g) was distilled to give 0.61 g of product bp 90°C, [illegible] μ. The molecular weight was 385.

g. Purification of 4,4-Bis(difluoramino)pentanoic Acid

The previously isolated* crude 4,4-bis(difluoramino)-pentanoic acid was treated to remove the contaminant, 5,5-dinitro-2,2-bis(difluoramion)pentane. The impure acid was dissolved in a 10% solution of sodium hydroxide and a slight excess of sodium hypochlorite (3% solution) was added. The solution was extracted with methylene chloride then acidified with sulfuric acid. The solution was again extracted with methylene chloride and the organic layer was dried over sodium sulfate. The solvent was stripped off and the remainder was purified by molecular distillation.

Anal. Calcd. for $C_5H_8N_2F_4O_2$: C, 29.4; H, 3.92; N, 13.7; F, 37.2. Found C, 29.8; H, 4.13; N, 13.4; F, 36.0.

*Aerojet-General Report 0235-01-17, June 1963, p. 7 (Confidential).

B. AQUEOUS FLUORINATION (V. Grakauskas)

1. Discussion

a. Amides

Early attempts to fluorinate primary amides lead to inconclusive results.* To determine whether unstable fluoramine is formed the fluorination of acetamide was attempted in the presence of cyclohexanone,** which has been shown to react with fluoramine to give ϵ-caprolactam.*** The reaction products, however, were identified as methylamine and ϵ-caprolactone. The formation of methylamine can be rationalized by the Hofmann rearrangement of N-fluoroacetamide:

$$CH_3CONH_2 + F_2 \xrightarrow{(H_2O)} CH_3CONHF \xrightarrow{-HF} \left[CH_3CON:\right] \xrightarrow{H_2O} CH_3NH_2 + CO_2$$

An interesting feature of this reaction is that it takes place in an acidic medium, although a base is required when other halogens are used to effect the Hofmann rearrangement.

ϵ-Caprolactone was found to be produced from the fluorination of aqueous cyclohexanone in the absence of acetamide, under either acidic or basic reaction conditions. The formation of lactones irom ketones by the action of Caro's acid or related peroxygen compounds is well known.**** It is possible that the above transformation is caused by either hydrogen peroxide or ozone, both of which are known to be produced in low concentration from fluorine and water. Another possible reactive species is hypofluorous acid, which might add to cyclohexanone; the loss of fluoride ion and rearrangement would give ϵ-caprolactone:

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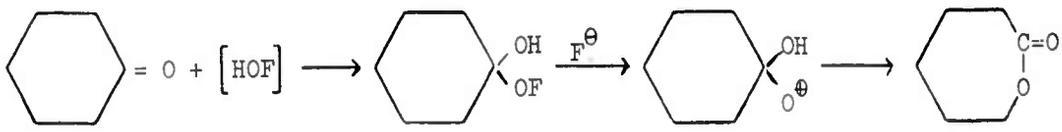
*Aerojet-General Report No. 2099 (Annual Summary), November 1961, p. 21 (Confidential).

**Aerojet-General Report No. 0235-01-16, March, 1963, p. 14 (Confidential).

***Aerojet-General Report No. 2381 (Annual Summary), October 1962, p. 33 (Confidential).

****For a brief review see W. von Doering and L. Speers, J. Am. Chem. Soc., 72, 5515 (1950); R. J. Kennedy and A. M. Stock, J. Org. Chem., 25, 1901 (1960).

$$F_2 + H_2O \longrightarrow [HOF] + HF$$



The fluorination of cyclohexanecarboxylic acid amide* supplied additional evidence that N-fluoroamides undergo the Hofmann rearrangement. In this reaction, in addition to cyclohexylamine, some cyclohexyl isocyanate (the Hofmann rearrangement intermediate) was isolated. The aqueous fluorination of formamide** gave N,N-difluorourea, apparently by Hofmann rearrangement to give cyanic acid, hydration to urea, and fluorination of the latter:

$$HCONH_2 \xrightarrow[F_2]{(H_2O)} HNCO \xrightarrow{(H_2O)} NH_2CONH_2 \xrightarrow{F_2} NF_2CONH_2$$

The fluorination of aqueous N-2-hydroxyethyl-acetamide gave only a trace of the expected product, β-difluoraminoethanol. The main reaction product was identified as β-difluoraminoethyl acetate (20% yield). The ester could be produced from a cyclic hemiacetal intermediate:

$$CH_3CONHCH_2CH_2OH + F_2 \xrightarrow{(H_2O)} CH_3CONFCH_2CH_2OH \longrightarrow HO\text{-}C(CH_3)(NF\text{-}CH_2)\text{-}O\text{-}CH_2 \xrightarrow[(H_2O)]{F_2} CH_3COOCH_2CH_2NF_2$$

β-Difluoraminoethyl acetate was identified by its infrared spectrum (Figure 24), its proton (Figure 25) and F^{19} (Figure 26) NMR spectra, and by its elemental analysis. A small amount of β-difluoraminoethyl fluoroacetate, $CH_2FCOOCH_2CH_2NF_2$, was also isolated and was identified by its elemental analysis and its proton (Figure 27) and F^{19} (Figure 28) NMR spectra.

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*Aerojet-General Report 0235-01-16, March 1963, p. 15 (Confidential).

**Aerojet-General Report 0235-01-17, June 1963, p. 9 (Confidential).

The fluorination of aqueous N-2-hydroxyethylformamide similarly gave β-difluoraminoethyl formate (25% yield) contaminated with a small amount of β-difluoraminoethanol. β-Difluoraminoethyl formate was identified on the basis of its infrared spectrum (Figure 29) and its elemental analysis.

$$HCONHCH_2CH_2OH + F_2 \xrightarrow{(H_2O)} HCOOCH_2CH_2NF_2$$

One attempt to generate β-difluoraminoethanol by hydrolysis of the acetate with 50% aqueous sulfuric acid failed, probably because of the instability of the alcohol under these reaction conditions. However, β-difluoraminoethanol was obtained in 70-75% yields by transesterification of its formate or acetate ester with methanol:

$$HCOOCH_2CH_2NF_2 + CH_3OH \xrightarrow[\Delta]{(H_2SO_4)} NF_2CH_2CH_2OH + HCOOCH_3$$

β-Difluoraminoethanol was characterized by its elemental analysis, its infrared spectrum (Figure 30), and its proton (Figure 31) and F^{19} (Figure 32) NMR spectra.

The ethyl ester of difluoraminoacetic acid was obtained in the fluorination of aqueous ethyl N-carbomethoxyglycine:

$$\begin{matrix} NHCH_2COOC_2H_5 \\ | \\ COOCH_3 \end{matrix} + F_2 \xrightarrow{(H_2O)} NF_2CH_2COOC_2H_5$$

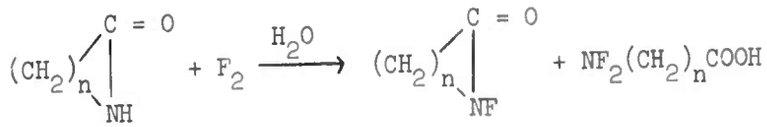
The compound could not be separated completely by fractional distillation or gas chromatography from its dehydrofluorination product, ethyl cyanoformate. The crude compound was characterized by elemental analysis, its infrared spectrum (Figure 33), and its proton (Figure 34) and F^{19} (Figure 35) NMR spectra. Ethyl difluoraminoacetate, ethyl cyanoformate, and ethyl N,N-difluorohydantoate was obtained in the fluorination of ethyl hydantoate. The latter

compound was identified on the basis of its elemental analysis and its proton and F^{19} NMR spectra (Figures 36 and 37).

$$NH_2CONHCH_2COOC_2H_5 + F_2 \xrightarrow{(H_2O)} NF_2CH_2COOC_2H_5 + NF_2CONHCH_2COOC_2H_5 + NCCOOC_2H_5$$

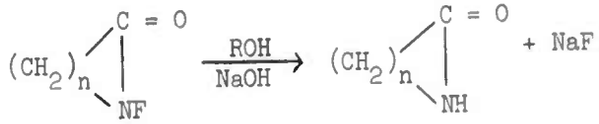
b. Lactams

The fluorination of aqueous 2-pyrrolidinone and ϵ-caprolactam has been reported* to give the corresponding ω-difluoraminocarboxylic acids in good yields. The use of less fluorine resulted in the isolation of the corresponding N-fluorolactams in addition to the ω-difluoraminocarboxylic acids:**



n = 3 or 5

These N-fluorolactams reacted with ethanolic sulfuric acid to form ammonium sulfate and unidentified organic products. They were not attacked by cold aqueous sodium bicarbonate, but underwent rapid decomposition even at 0 to 5°C when treated with dilute aqueous alkali. Alcoholic alkali decomposed them to the corresponding lactams and alkali fluorides.



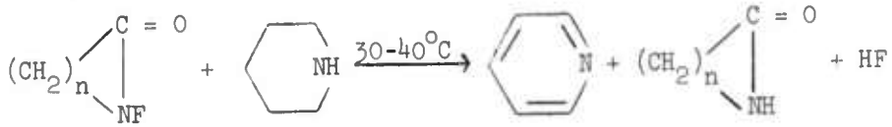
Several attempts were made to use N-fluorolactams as fluorinating agents,*** as N-bromocaprolactam is used as a brominating

*Aerojet-General Report 2381 (Annual Summary), p. 21, October 1962 (Confidential).

**Aerojet-General Report 0235-01-15, January 1963, p. 14 (Confidential).

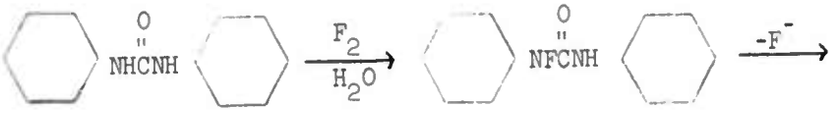
***Aerojet-General Report 0235-01-15, January 1963, p. 15 (Confidential).

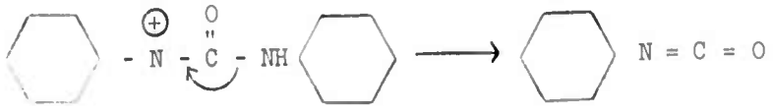
agent.* Cyclohexene did not react with either N-fluoro-2-pyrrolidinone or N-fluorocaprolactam in the presence of benzoyl peroxide at elevated temperatures. Attempts to transfer fluorine from N-fluorolactams to either urea or ethyl methylcarbamate also failed, and only the starting materials were recovered after heating the corresponding mixtures of reagents at 85 to 95°C for several hours. However, piperidine reacted with both N-fluorolactams to give small amounts of pyridine and the corresponding unsubstituted lactams:



c. Ureas

In a search for a better synthesis route to cyclohexyldifluoramine, the fluorination of aqueous N,N'-dicyclohexylurea was investigated.** The fluorination product, however, was identified as cyclohexylisocyanate, produced by an unusual C-N cleavage of the N-fluoro intermediate, such as the following:





A similar reaction was observed in the fluorination of cyclohexylurea.*** The products of this reaction were cyclohexyl isocyanate, difluoraminocyclohexane and N,N-difluorocyclohexylurea:

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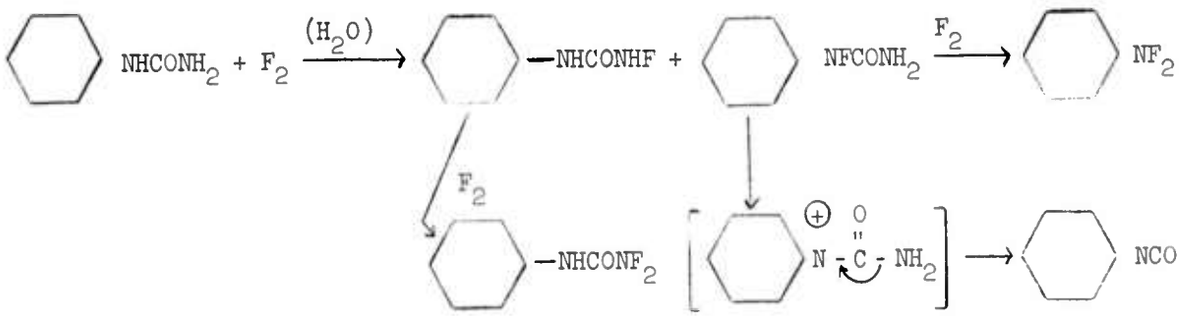
*B. Taub and J. B. Hino, J. Org. Chem., 25, 263 (1960); H. Beyer and J. Korosi, Ber., 94, 480 (1961).

**Aerojet-General Report 0235-01-15, January 1963, p. 16 (Confidential).

***Aerojet-General Report 0235-01-16, March 1963, p. 16 (Confidential).



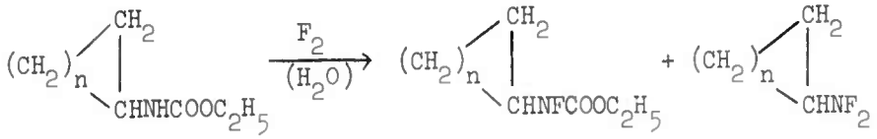
d. Carbamates

The preparation of 1,3-bis(difluoramino)propane by the fluorination of aqueous ethyl trimethylenedicarbamate resulted in only a 3% yield.* Since larger quantities of the material are required for sensitivity studies, other methods of preparation were investigated. The fluorination of aqueous methyl trimethylenedicarbamate was found to give crude 1,3-bis(difluoroamino)propane (85% purity) in 13 to 15% yields. The higher solubility of methyl trimethylenedicarbamate, compared to the ethyl derivative, could account for the increased yield. A contaminant of the product was isolated by gas chromatography and identified as 1,3-bis(difluoramino)-1-fluoropropane on the basis of its infrared spectrum, elemental analysis, and its proton (Figure 38) and F^{19} (Figure 39) NMR spectra. In addition to 1,3-bis(difluoramino)propane, larger quantities (40 to 50% yield) of intermediates, $NF_2CH_2CH_2CH_2NFCOOCH_3$ and $CH_2(CH_2NFCOOCH_3)_2$, were isolated. It appears that further fluorination is prevented by insolubility of the intermediates in water. Other solvents will be investigated.

The fluorination of sodium bicarbonate buffered 1,3-diaminopropane, N,N'-diformyl-3,3-diaminopropane, and N,N'-diacetyl-1,3-diaminopropane were also investigated, but desired product was not obtained in the first case and only 3 to 5% yields of 1,3-bis(difluoroamino)propane were obtained using the acyl derivatives.

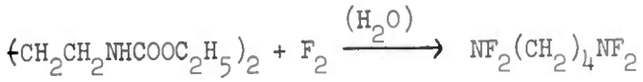
*Aerojet-General Report 2381, October 1962, p. 19 (Confidential).

The fluorination of ethyl cyclopentylcarbamate and ethyl cyclohexylcarbamate gave the corresponding difluoramines in 10 to 20% yields, in addition to 10 to 25% yields of the N-fluorocarbamates:*



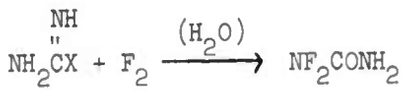
n = 3 or 4

Diethyl tetramethylenedicarbamate was also fluorinated to give 1,4-bis(difluoramino)butane (10% yield), and several partially fluorinated intermediates.**



e. Miscellaneous

Some attempts were made to synthesize perfluoramidine derivatives by the fluorination of amidines. The fluorination of methylisourea sulfate (X=OCH_3) and aminoiminomethanesulfinic acid (X=SO_2H), however, yielded N,N-difluorourea, apparently as a result of the hydrolysis of partially fluorinated intermediates.***



The fluorination of aqueous ethyl azodicarboxylate and ethyl hydrazodicarboxylate was investigated with the objective of synthesizing N-fluorohydrazine derivatives. Fluorine was readily consumed in both reactions, but no NF compounds were produced. Instead, in both cases, the reaction product was identified (elemental analysis and NMR spectrum) as tricarbethoxy-hydrazine:

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*Aerojet-General Report 0235-01-15, January 1963, p. 16 (Confidential).

**Aerojet-General Report 0235-01-16, March 1963, p. 17 (Confidential).

***Aerojet-General Report 0235-01-17, June 1963, p. 9 (Confidential).

$$(NHCOOC_2H_5)_2 \text{ or } (NCOOC_2H_5)_2 \xrightarrow[CH_2O]{F_2} \begin{matrix} NHN(COOC_2H_5)_2 \\ | \\ COOC_2H_5 \end{matrix}$$

The course of the reactions is unknown.

The fluorination of aqueous 5-aminotetrazole was also investigated. Fluorine was consumed in this reaction. The only product isolated was hydrogen cyanide, indicating decomposition of tetrazole ring.

The reaction of ethyl N-fluorocarbamate with phosphorous pentachloride previously gave a complex mixture which was not identified.* The reaction between methyl N-fluorocarbamate and phosphorous pentoxide** at 65 to 75°C produced a white solid, tentatively identified as methyl N,N-difluoro-allophanate. The allophanate may be formed by the in situ reaction of FNCO with N-fluorocarbamate, or by a simple condensation:

$$NHFCOOCH_3 \xrightarrow[\Delta]{P_2O_5} NHFCONFCOOCH_3$$

Since this compound is of interest for fluorination studies, attempts were made to improve the yield of the material. However, when a mixture of methyl N-fluorocarbamate and phosphorous pentoxide was heated to 100°C, the mixture fumed off, and when gaseous carbamate was passed through hot phosphorous pentoxide, no reaction occurred, even at 170°C. The use of thionyl chloride as a dehydrating agent did not give the allophanate.

Methyl N-fluorocarbamate was found to react readily with hydrogen chloride at ambient temperature with the formation of ammonium fluoride.**

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*Aerojet-General Report 2099 (Annual Summary), November 1961, p. 31 (Confidential).

**Aerojet-General Report 0235-01-17, June 1963, pp. 10-11 (Confidential).

2. Experimental

a. β-Difluoraminoethyl Acetate

A solution of 103 g (1.0 mole) of N-acetylethanolamine (practical grade) in 650 ml water was fluorinated at 0 to 5°C until 45 liters of fluorine was consumed. The reaction mixture was extracted with five 40-ml portions of methylene chloride. The combined methylene chloride extracts were dried, deacidified with solid sodium bicarbonate, filtered and the filtrate concentrated to remove the solvent. The residual liquid was distilled to give 23 g of a colorless liquid bp 40-50°C/25 mm, n_D^{23} 1.3740, which was found (gas chromatography) to contain 15% difluoraminoethanol and 80% of β-difluoraminoethyl acetate. An analytical sample of the pure ester was obtained by gas chromatography.

Anal. Calc'd for $C_4H_7NF_2O$: C, 34.54; H, 5.07; N, 10.07; F, 27.3.

Found: C, 34.4; H, 5.16; N, 9.87; F, 27.8.

The infrared spectrum of the compound is shown in Figure 24.

The sample for NMR was obtained in the form of a gas chromatography fraction. The 60-mc proton NMR spectrum (Figure 25) was obtained using carbon tetrachloride solution with TMS added as an internal reference and employing a Varian Microcell. The 2.04-ppm signal is assigned to the acetate methyl, the triplets of triplets (14 cps, 222 cps and, in part, 255 cps) to the methylene adjacent to NF_2, and the 255 cps multiplet (in part) to the methylene adjacent to the oxygen.

The 56.4-mc F^{19} NMR spectrum (Figure 26) was obtained using the same sample with Freon-11 added as an interval reference. The spectrum consists of a single peak, a triplet (splitting 25 cps) at -3078 cps (-54.57 ppm). The triplet is assigned to the difluoramino group.

The proton and F^{19} NMR spectra are consistent with each other and with the structure $CH_3COOCH_2CH_2NF_2$.

b. β-Difluoraminoethyl Fluoroacetate

After removal of β-difluoraminoethyl acetate (above), the residual liquid was fractionated further to give 5.0 g of colorless liquid, bp 29-30°C/0.1 mm, n_D^{24} 1.3900. This material was analyzed by gas chromatography and was found to contain two compounds. The first component, present in 70% concentration in the mixture contained no NF and was not identified. The second component, present in 28% concentration, was identified as β-difluoraminoethyl fluoroacetate, $CH_2FCOOCH_2CH_2NF_2$.

Anal. Calc'd for $C_4H_6NF_3O_2$: C, 30.6; H, 3.85; N, 8.92; F, 36.3.
Found: C, 31.0; H, 3.65; N, 9.67; F, 35.5.

The 60-mc proton NMR spectrum (Figure 27) was obtained using carbon tetrachloride solution with TMS added as an internal reference and employing a Varian microcell. The spectrum consists of three irregular triplets (centered at approximately 200, 227, and 255 cps), another irregular triplet (centered at approximately 275 cps), and a sharp doublet (splitting 46.4 cps) centered on 4.83 ppm.

The 56.4-mc F^{19} NMR spectrum (Figure 28) consists of a broadened triplet (splitting 27.0 cps) at -3057 cps (-54.2 ppm) and sharper, well resolved triplet (splitting 46.7 cps) at +13,067 cps (+231.68 ppm).

The proton and fluorine NMR spectra can be rationalized on the basis of the structure $NF_2CH_2CH_2OOCCH_2F$. In the fluorine spectrum the -54.2 ppm triplet is assigned to the difluoramino group, and the +231.68 ppm triplet to the fluorine, $-CH_2\underline{F}$. In the proton spectrum the irregular triplets at 200, 227, and 255 cps are assigned to the NF_2 substituted methylene, $NF_2\underline{CH_2}CH_2$-. The triplet at 275 cps is assigned to the methylene adjacent to oxygen, $-\underline{CH_2}CH_2O$-, and the doublet to the $-\underline{CH_2}F$ methylene group.

c. β-Difluoraminoethyl Formate

A solution of 44.5 g (0.5 mole) of N-formylethanolamine (practical grade) in 350 ml water was fluorinated at 0 to 5°C until 23 liters of fluorine was consumed (in 2 hours). The reaction mixture was extracted

with five 25-ml portions of methylene chloride, the combined extracts dried, deacidified with solid sodium bicarbonate, filtered and concentrated to remove the solvent. The residual liquid was distilled to give 17.5 g of material, bp 38-45°C/25 mm, n_D^{25} 1.3720. Distillation residue, amounting to 2.1 g was discarded. The material (analyzed by gas chromatography) contained 11% of β-difluoraminoethanol and 89% β-difluoroaminoethyl formate. An analytical sample of the latter was obtained by gas chromatography.

Anal. Calc'd for $C_3H_5NF_2O_2$: C, 28.8; H, 4.03; N, 11.2; F, 30.4.
Found: C, 28.7; H, 4.15; N, 11.2; F, 30.4.

The infrared spectrum of the compound is shown in Figure 29.

d. β-Difluoraminoethanol

To a solution of 14.5 g of β-difluoraminoethyl acetate in 40 ml of methanol was added two drops of concentrated sulfuric acid and the mixture reacted for a period of 3.0 hours. The solution was cooled to room temperature and concentrated at 25-mm pressure to remove methanol and methyl acetate. The residual liquid was flash-distilled at 0.1 mm pressure. The material was redistilled to give 5.0 g of a colorless liquid, bp 40-42°C/25 mm, n_D^{25} 1.3685. The material was analyzed by gas chromatography and contained 91% β-difluoraminoethanol and 6% of the acetate. An analytical sample of the alcohol was obtained by gas chromatography.

Anal. Calc'd for $C_2H_5NF_2O$: C, 24.74; H, 5.16; N, 14.44; F, 39.15.
Found: C, 24.6; H, 5.3; N, 14.3; F, 38.5.

The infrared spectra of the material is given in Figure 30.

The 60-mc proton NMR spectrum (Figure 31) was obtained using $CDCl_3$ solution, with TMS added as an internal reference, by means of a Varian microcell. The intense singlet of 2.25 ppm is assigned to the hydroxyl proton. The multiplets of 192 cps and 226 cps are assumed to be the two high field members of a triplet of triplets assignable to the methylene adjacent

to the NF_2 group. The multiplet at 239 cps is then assigned to the overlapping low field member of the triplet of triplets and the signal assignable to the methylene adjacent to oxygen.

The 56.4-mc F^{19} NMR spectrum (Figure 32) was obtained using Freon-11 as an internal reference. The spectrum consists of a single signal a broadened, poorly resolved triplet (splitting 26 cps) at -3095 cps (-54.88 ppm). The triplet may be assigned to the $N\underline{F}_2CH_2CH_2OH$ difluoramino group.

The proton and F^{19} NMR spectra are generally consistent with the structure. However, the complexity of the proton spectrum which is a consequence of the similarity of the chemical shifts makes any conclusion as to the structure somewhat tentative.

A solution of 29 g of β-difluoraminoethyl formate in 40 ml of dry methanol containing 2 drops of concentrated sulfuric acid was heated up to 55 to 60°C and maintained at this temperature. During this time methyl formate-methanol azeotrope was distilled off. After 2 hours of heating, when no more azeotropic mixture distilled over, the reaction mixture was cooled to 25 to 30°C and methanol distilled over at 25 mm pressure. The residual material was distilled to give 18 g of a colorless liquid, bp 40-42°C/25 mm, n_D^{24} 1.3645. The material was found to be 90% pure β-difluoraminoethanol (gas chromatograph) corresponding to 70% yield.

e. Ethyl Difluoraminoacetate

A solution of 48.3 g (0.3 mole) of ethyl N-carbomethoxyglycine in 650 ml water was fluorinated at 0 to 5°C until 14 liters of fluorine was consumed (75 min). The reaction mixture, containing 5 to 6 ml of heavy water insoluble liquid, was extracted with five 40 ml portions of methylene chloride. The combined methylene chloride extracts were dried, deacidified with solid sodium bicarbonate, filtered, and concentrated. The residual liquid was fractionated to give 7.5 g of colorless liquid, bp 33-35°C/25 mm, n_D^{23} 1.3780 which was identified as ethyl cyanoformate, on the

basis of its physical constants (lit.* bp 115-116°C, n_D^{20} 1.3818) and its infrared spectrum. The material was not pure and contained some of ethyl difluoraminoacetate. Further fractionation gave 3.5 g of a colorless liquid, bp 40-42°C/25 mm, n_D^{25} 1.3760 which, as determined by gas chromatography, contained 20% ethyl cyanoformate and 80% ethyl difluoraminoacetate. A difficulty arose in obtaining a pure sample of the acetate by gas chromatography. At 60 to 70°C, using a variety of column materials, the compound apparently underwent some dehydrofluorination and formed considerable amounts of cyanoformate. Because of this difficulty, elemental analysis, infrared, and NMR spectra were obtained using material containing some cyanoformate.

Anal. Calc'd for $C_4H_7NF_2O_2$: C, 34.54; H, 5.07; N, 10.07; F, 27.3.
Found: C, 32.5; H, 5.2; N, 10.6; F, 27.0.

Infrared spectrum of the material is shown in Figure 33.

The 60-mc proton NMR spectrum (Figure 34) was obtained using carbon tetrachloride solution with TMS added as an internal reference. The assignments for the proton spectrum are as follows. The intense triplet at 1.32 ppm and the quartet at 4.24 ppm (overlapped by other signals) are assigned to the carbethoxy ethyl group. The triplet (splitting 28 cps) at 4.24 ppm (the same chemical shift as the ethyl group quartet) is assigned to the $NF_2C\underline{H}_2O$-methylene. Two relatively weak triplets of about equal intensity appear at 1.38 and 1.40 ppm. Additional weak signals appear to the low field side of the 4.24 ppm triplet and quartet. They appear to be the low field members of two quartets centered at about 262 cps. The triplets and quartets indicate the presence of two impurities of about equal concentration and each containing an ethyl group. Two other weak signals are also evident.

The proton spectrum thus indicates that the material is roughly 70% pure.

*W. Wallach, Ann., 184, 12 (1872).

The 56.4-mc F^{19} NMR spectrum (Figure 35) was obtained using the same sample with Freon-11 added as an internal reference. The spectrum consists of a single signal, a broadened, rather poorly resolved triplet (splitting 26 cps) at -3181 cps (-56.40 ppm). The signal is assigned to the $\underline{NF_2}CH_2$-difluoramino group.

After removal of ethyl cyanoformate and ethyl difluoraminoacetate, the residual liquid was distilled to give 6.0 g of a colorless liquid, bp 50-51°C/0.1 mm n_D^{25} 1.4030, which on the basis of its infrared spectrum was tentatively identified as N-fluoro derivative of the starting material. Its characterization, however, is not completed.

Ethyl difluoraminoacetate was also obtained in the fluorination of ethyl hydantoate. A solution (partially in suspension) of 73 g (0.5 mole) of ethyl hydantoate in 650 ml of water was fluorinated at 0 to 5°C until 23 liters of fluorine was consumed (2.0 hours). At the end of the fluorination the reaction mixture, containing 10 to 12 ml of heavy liquid, was extracted with five 50-ml portions of methylene chloride. The combined methylene chloride extracts were dried, deacidified with solid sodium bicarbonate, filtered, and concentrated to remove the solvent. The residual material was fractionated to give 9.5 g of a colorless liquid, bp 32-35°C/25 mm which, as determined by gas chromatography and infrared spectrum, contained 55% of ethyl cyanoformate and 45% of ethyl difluoraminoacetate. Another fraction of the mixture, bp 38-42°C/25 mm (6.5), containing 25% of the formate and 75% of difluoraminoacetate was obtained on further fractionation.

f. Ethyl N,N-Difluorohydantoate

After removal of ethyl cyanoformate and difluoraminoacetate, further distillation of the reaction product (see above) gave 15 g of a colorless liquid bp 66-67°C/0.1 mm, n_D^{23} 1.4188, which was identified as ethyl N,N-difluorohydantoate.

Anal. Calc'd for $(C_5H_8N_2F_2)_3$: C, 33.0; H, 4.4; N, 15.4; F, 20.9

Found: C, 33.0; H, 4.5; N, 15.5; F, 20.7.

The 60-mc proton NMR spectrum (Figure 36) was obtained using carbon tetrachloride solution with TMS added as an internal reference. The assignments are as follows. The triplet at 1.31 ppm and the quartet at 4.20 ppm (overlapped by another signal) are assigned to the methyl and methylene of the ethyl group, respectively. The doublet at 3.99 ppm (overlapped by the quartet) is assigned to the -NHC$\underline{H}_2$CO-methylene. The broadened signal at 7.09 ppm is assigned to the amide proton.

The 56.4-mc F^{19} NMR spectrum (Figure 37) was obtained using the same sample with Freon-11 added as an internal reference. The spectrum consists of single, somewhat broadened signal at -1828 cps (-32.4 ppm). It is assigned to the N$\underline{F}_2$CO- group.

The proton and fluorine spectra are consistent with the structure.

g. 1,3-Bis(difluoramino)propane

A solution of 19 g (0.1 mole) of dimethyl trimethylenedicarbamate in 350 ml of water was fluorinated at 0 to 5°C until 9 liters of fluorine was consumed (1 hour, 15 min). At the end of the run the reaction mixture containing 3 to 5 ml of pale-yellow liquid was extracted with four 25-ml portions of methylene chloride. The combined methylene chloride extracts were dried, deacidified with solid sodium bicarbonate, filtered, and concentrated at 15 to 18°C/25 mm to remove methylene chloride. The residual liquid was fractionated to give

2.8 g of liquid, bp 26-43°C/25 mm
7.2 g of liquid, bp 40-48°C/0.1 mm
1.0 g of liquid, bp 55-75°C/0.1 mm
Distillation residue, 1.9 g, discarded.

The material of the fourth fraction was analyzed by gas chromatography and contained 78% of 1,3-bis(difluoramino)propane, equivalent to 15% yield. The compound was contaminated with five impurities ranging from 3 to 8.5%.

The higher boiling products were not identified, but on the basis of their boiling points the material or fraction 2 is probably mainly $NF_2CH_2CH_2CH_2NFCOOCH_3$, and that of fraction 3, $CH_2(CH_2NFCOOCH_3)_2$.

Identical results were obtained when the fluorination was repeated using 0.2 mole of the starting material.

A solution of 26 g (0.2 mole) of N,N'-diformyl-1,3-diaminopropane in 350 ml of water was fluorinated at 0 to 5°C until 18 liter of fluorine was consumed. At the end of the run the reaction mixture was extracted with four 20-ml portions of methylene chloride, the combined extracts dried, deacidified, filtered and worked up to give 2.5 g of a colorless liquid, bp 26-30°C/25 mm, which contained 55% of 1,3-bis(difluoramino)propane (5% yield) as determined by gas chromatography. In addition the mixture contained another major component present in 33% concentration, and four other impurities present in 1 to 3% concentration.

h. 1,3-Bis(difluoramino)-1-fluoropropane

The major component present in the crude 1,3-bis-(difluoramino)propane (see above) was separated by gas chromatography and identified as 1,3-bis(difluoramino)-1-fluoropropane, $NF_2CHFCH_2CH_2NF_2$.

Anal. Calc'd for $C_3H_5N_2F_5$: C, 22.0; H, 3.1; N, 17.1; F, 57.9.
Found: C, 21.2; H, 3.3; N, 16.2; F, 56.2.

The 60-mc proton NMR spectrum (Figure 38) was obtained using carbon tetrachloride solution with TMS added as an internal reference in a Varian microcell. The assignments are as follows. The triplet (splitting 27.6 cps) of triplets centered on 3.73 ppm is assigned to the $NF_2C\underline{H}_2CH_2$-methylene. The wide symmetrical multiplet centered on 5.45 ppm may be assigned to the $-CH_2C\underline{H}FNF_2$ proton. On the first order basis, this multiplet would be expected to contain 18 components; i.e., the signal would be split into a doublet by fluorine on the same carbon, further into triplets by the $-NF_2$ fluorines, and again into triplets by the adjacent $-CH_2-$ group. The

multiplet corresponds at least roughly to the expected form although the low signal-to-noise ratio makes any further analysis difficult. This leaves the multiplet with its maximum intensity at 1.36 cps to be assigned to the central methylene $-CH_2\underline{CH_2}CHF-$. On the first order basis the signal would be expected to be a pair of quartets. The signal corresponds only very roughly to this form. This may result from the asymmetry of the -CHF-carbon.

The 56.4-mc F^{19} NMR spectrum (Figure 39) was obtained, using the same sample with Freon-11 added as an internal reference. The broadened, poorly resolved triplet at -3010 cps (-53.37 ppm) is assigned to the NF_2CH_2- fluorines. The splitting observed is 25 cps in rather poor agreement with the probably more reliable 27.6 cps value obtained from the proton spectrum. The nonequivalence quartet (chemical shifts at -29.2 and -19.3 ppm, coupling constant 610 $\pm$4 cps) is assigned to the $-CHF\underline{NF_2}$ fluorines. The doublet (51 cps) of triplets (19 cps) at +9781 cps (+173.41 ppm) is assigned to the $-CH_2\underline{CH}F-$ fluorine. The proton and fluorine NMR spectra are generally consistent with each other and with the $NF_2CH_2CH_2CHFNF_2$ structure, although some of the details of the proton spectrum are obscure. The other possible fluorination product, $NF_2CH_2CHFCH_2NF_2$ is clearly excluded.

i. Fluorination of Diethyl Azodicarboxylate

A suspension of 43 g (0.25 mole) of diethyl azodicarboxylate in 1000 ml water was fluorinated at 0 to 5°C until 6 liters of fluorine was consumed. No volatile products accumulated in two -80°C traps connected in series with the reactor. At the end of the run the reaction mixture was extracted with four 50-ml portions of methylene chloride and the extracts were worked up to give 25 g of pale-yellow very viscous oil, bp > 140°C/0.1 mm. A portion of this material was distilled in a molecular still at 150 to 155°C pot temperature at 0.1 mm. The material was identified as tricarbethoxyhydrazine on the basis of its infrared spectrum, its elemental analysis (calc'd: N, 11.3%; found: N, 11.3%) and proton NMR spectrum. Furthermore, its physical constants are in agreement with those reported in the literature.*

*O. Diels and E. Borgwardt, Ber., 53B, 150 (1920).

j. Fluorination of Diethyl Hydrazodicarboxylate

Tricarboethoxyhydrazine was the sole reaction product isolated in the fluorination of aqueous diethyl hydrazodicarboxylate. The fluorination was carried out as described above.

C. FLUORAMMONIUM SALTS (A. Remanick, V. Grakauskas)

1. Discussion

Hydrolysis of ethyl N-fluorocarbamate with concentrated sulfuric acid, followed by quenching with aqueous cyclohexanone gave caprolactam. Apparently fluoramine was formed and added to the ketone to give an intermediate which underwent a Beckmann rearrangement. The NMR spectrum of the sulfuric acid solution also was consistent with the fluorammonium cation.* This work was continued with the aim of isolating and characterizing fluorammonium salts which are potentially valuable as solid oxidizers.

It was found that heating ethyl N-fluorocarbamate with concentrated sulfuric acid, followed by dilution with ether, gave a white, hygroscopic solid.** Elemental and NMR analysis of this salt indicated the fluorammonium cation and the anions, $HSO_4^{\ominus}$, $CH_3CH_2OSO_3^{\ominus}$ and $HOCH_2CH_2SO_3^{\ominus}$.

The salt was stable for several days at room temperature under anhydrous conditions, although it decomposed rapidly at 90°C. It was unstable in hydroxylic solvents and insoluble in other common organic solvents. Reprecipitation from concentrated sulfuric acid did not improve its purity.***

The reaction of sulfuric acid with excess methyl N-fluorocarbamate gave a material with an elemental analysis approximating that of fluorammonium bisulfate.**** However, this reaction was difficult to repeat.

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*Aerojet-General Report No. 2381, October 1962, p. 32 (Confidential).

**Aerojet-General Report No. 0235-01-16, March 1963, p. 21 (Confidential).

***Aerojet-General Report No. 0235-01-17, June 1963, p. 15 (Confidential).

The reaction of ethyl N-fluorocarbamate with excess methanesulfonic acid gave a white, crystalline solid which was shown by elemental analysis to be fluorammonium methanesulfonate. A semiquantitative KI titration, and infrared (Figure 40) and NMR spectra (see the Experimental Section), also agreed with this assignment. The yield was 50 to 60%.

The material is relatively inert to impact (>150 cm/2Kg) and electrostatic charge (positive at 5 joules, negative at 2.5 joules). It does not appear to be very hygroscopic although it reacts with moisture on exposure to air. It is stable for several days at room temperature in an inert atmosphere but decomposes rapidly at 105 to 110°C.

The solubility characteristics of fluorammonium methanesulfonate were investigated with the intention of finding a solvent for metathetical reactions. The material was insoluble and/or unstable in most common solvents. However, the salt could be recovered quantitatively from a solution in trifluoracetic acid which had been maintained at room temperature for 1 hour; after longer periods, there was evidence of decomposition. The salt could also be recovered quantitatively from methanol solution after standing at -78°C for 1 hour. It was also found that from a nearly saturated solution in 60% perchloric acid at room temperature a small amount of the methanesulfonate crystallized on standing 18 hours at -20°C.

The following metathetical reactions were attempted in order to prepare the fluorammonium salts of other anions:

$$2FNH_3CH_3SO_3 + Ba(CF_3CO_2)_2 \xrightarrow[25^\circ]{CF_3CO_2H} 2FNH_3\,CF_3CO_2 + \underline{Ba(CH_3SO_3)_2}$$

$$2FNH_3CH_3SO_3 + Ba(ClO_4)_2 \xrightarrow[80^\circ]{MeOH} 2FNH_3ClO_4 + \underline{Ba(CH_3SO_3)_2}$$

$$FNH_3CH_3SO_3 + AgClO_4 \xrightarrow[-80^\circ]{MeOH} FNH_3ClO_4 + \underline{Ag\,CH_3SO_3}$$

$$FNH_3CH_3SO_3 + NaClO_4 \xrightarrow[-80^\circ]{MeOH} FNH_3ClO_4 + \underline{NaClO_4}$$

These reactions did not lead to the desired product. Decomposition of the fluorammonium cation was indicated by the lack of oxidizing power in the recovered products.

Since a metathesis scheme was not successful in the preparation of fluorammonium perchlorate, the direct reaction of perchloric acid with an alkyl N-fluorocarbamate was investigated as an alternate method. The reaction of methyl-N-fluorocarbamate with excess 70% perchloric acid proceeded to about 25% completion (as measured by carbon dioxide evolution) at 50°C in about 2 hours. A slightly higher reaction temperature resulted in violent decomposition of the mixture. The use of isopropyl-N-fluorocarbamate with 70% perchloric acid markedly increased the reaction rate. As measured by carbon dioxide evolution, the reaction proceeded to 70% completion in 2 hours at 25 to 40°C. No solid could be recovered after unreacted starting materials were removed under vacuum. However, NMR investigation of the resulting liquid indicated the presence of an NF-containing material. This reaction is being investigated further.

2. Experimental

a. Fluorammonium Methansulfonate

A small amount [1.5 g (0.014 mole)] of ethyl N-fluorocarbamate was placed in a three-neck flask, equipped with a nitrogen inlet and magnetic stirrer, and connected to a gas burette. The system was flushed with nitrogen and 6.2 ml of methansulfonic acid was added. The reaction mixture was placed in a preheated bath (76°C) and heated to 90°C in 15 min. Gas evolution began about 8 min after the start of the heating. After 1 to 5 hours at 90 to 94°C, gas evolution had markedly diminished. At this time, ca. 50% of the theoretical amount of gas had evolved. Infrared analysis of the gas showed primarily CO_2 with traces of ethylene and silicon tetrafluoride. After this heating period, the reaction mixture was allowed to cool to room temperature. Ether was added dropwise, with stirring, until the reaction mixture was cloudy. After 1 hour, the solid was separated by filtration under nitrogen and was washed with ether. Traces of ether were removed under vacuum, leaving 1.05 g (57%) of white platelets.

Anal. Calc'd for $FNH_3CH_3SO_3$: C, 9.16; H, 4.58; N, 10.7; F, 14.5.
Found: C, 9.33; H, 4.77; N, 10.8; F, 14.6;
F (by KI), 12.3.

The infrared spectrum (Figure 40) was obtained using fluorolube (2 to 7.5 μ) and Nujol (7.5 to 16 μ) mulls. There was some reaction with the cell. The proton NMR spectrum in sulfuric acid contained a doublet at +0.25 ppm relative to sulfuric acid (FNH_3^+) and a singlet at +7.55 ppm (CH_3SO_3H). The F^{19} spectrum was identical to that of the previously reported fluorammonium spectrum salt.*

The salt was insoluble at 25 and 55°C in the following solvents: acetic acid, methyl N-fluorocarbamate, methyl formate, chloroform, and diglyme. The salt decomposed in a short time on contact with the following solvents at 25°C as evidenced by loss of oxidizing power: water, methanol, ethanol, acetone, dimethylsulfoxide, sulfolane, nitromethane, acetonitrile, and dimethylformamide. In the last four cases, vigorous reaction occurred.

b. Reaction of Fluorammonium Methanesulfonate with Barium Trifluoroacetate

To 3.0 ml of 2.41 M of fluorammonium methanesulfonate in trifluoracetic acid was added 4.15 ml of 0.868 M barium trifluoroacetate in trifluoracetic acid. The reaction mixture formed a thick gel. The voluminous solid was centrifuged and washed with trifluoracetic acid. Analysis of the solid showed essentially no nitrogen.

c. Reaction of Fluorammonium Methanesulfonate with Barium Perchlorate

In this experiment all operations were carried out at -78°C in a nitrogen atmosphere. To a sample of 0.3673 g (0.00280 mole) fluorammonium methanesulfonate was added 10 ml of precooled (-78°C) methanol and the mixture was stirred until solution was affected. To this solution was added 4.20 ml of 0.334 M barium perchlorate in methanol. A thick gel formed which decomposed when it was warmed to room temperature.

d. Reaction of Fluorammonium Methanesulfonate with Silver Perchlorate and with Sodium Perchlorate

A solution of 0.1698 g (0.00130 moles) fluorammonium methanesulfonate in 12 ml methanol was prepared at -78°C. The addition with stirring of 1.65 ml of 0.788 silver perchlorate in methanol caused a precipitate to form. Some fuming was noted during the addition. The mixture was filtered at -78°C and 35 ml precooled (-78°C) ether was added to the filtrate. A trace of material precipitated, which was shown to be silver perchlorate. The original precipitate was silver methanesulfonate. No oxidizing material was recovered.

In a similar manner, fluorammonium methanesulfonate was reacted at -78°C with an equivalent amount of sodium perchlorate. Although sodium methanesulfonate was precipitated, no oxidizing material could be recovered.

e. Reaction of Isopropyl N-Fluorocarbamate with 70% Perchloric Acid

In a three-neck flask which was connected to a gas burette was placed 0.89 g (0.00735 mole) isopropyl N-fluorocarbamate. The system was flushed with nitrogen and 3.0 ml (ca. 0.035 mole) 70% perchloric acid was added rapidly. Gas evolution commenced immediately. As measured by gas evolution, the reaction proceeded to 30% completion in 1 hour at room temperature. Slow heating to 40°C over a 1-hour period produced an additional 40% of the theoretical carbon dioxide. Infrared analysis of the product gas showed only carbon dioxide.

No solid could be isolated from the perchloric acid solution on removal of unreacted starting material under vacuum or on dilution with diglyme. NMR of residual material in 70% perchloric acid indicated the presence of an NF-containing material.

D. REACTIONS OF AZINE FLUORIDE (R. K. Robeson and A. F. Graefe)

1. Introduction

Preliminary results from experiments conducted at Aerojet-General* and elsewhere** indicated that azine fluoride, FN_3, is absorbed by solid potassium fluoride at ambient temperatures. This evidence suggested to us the possibility of formation of a new resonance-stabilized anion, $N_3F_2^{\ominus}$. Accordingly, a study of the azine fluoride-alkali metal fluoride system was undertaken to obtain data which would support the postulate. Particular attention was given to the poorest polarizing cations, potassium, rubidium, and cesium.

$$MF + FN_3 \longrightarrow M^+\left[FN\text{-}N{=}NF^{\ominus} \longleftrightarrow FN{=}N\text{-}NF^{\ominus}\right], \quad M = K, Rb, \text{ or } Cs$$

2. Discussion

a. Procedures

Although modifications in the original procedures of Haller were made, the procedures employed in the present program for the preparation and handling of azine fluoride were those utilized on the occasion when the FN_3-KF was first examined at Aerojet.*** Hydrazoic acid was generated by employing a melt of stearic acid and sodium azide. The azine fluoride from the vapor phase reaction of hydrazoic acid and fluorine, was collected in a calibrated trap containing Freon-11 maintained at -80°C, after passage through a 0°C trap to remove much of the accompanying hydrogen fluoride. Aliquots of the Freon-11 solution could be removed remotely and analyzed by iodimetric methods to obtain the amount of oxidizing materials present. The error to be expected from the solubility of fluorine in Freon-11 at -80°C under the conditions of the experiments was ascertained and was found to be very small - ca. 2×10^{-3} milliequivalents/milliliters of solution. To obtain FN_3 for subsequent reaction the Freon

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* Aerojet-General Report No. 1960, "Investigation of High-Energy Oxidizer Binders for Solid Propellants," February 1961 pg. 3 (Confidential).

** J. F. Haller, Dissertation, Cornell University Library, Ithaca, New York; Allied Chemical Corporation, Quarterly Progress reports PR-2, PR-3, July-December 1959 (Confidential).

*** Aerojet-General Report No. 1960, "Investigation of High-Energy Oxidizer Binders for Solid Propellants," February 1961, p. 18 (Confidential).

trap, fitted with a condenser through which coolant at -78° was circulated, was allowed to warm while helium was bubbled through the solution at a rate of about 2 liters/hour.

Evidence for the formation of azine fluoride consisted of the method of preparation, the usual chartreuse coloration of azine fluoride solutions, and the infrared spectrum which showed absorption bands at about 4.6, 4.90 and 4.95 μ. The spectrum indicated that other materials accompanied the azine fluoride purged from Freon-11 in the manner outlined; Freon-11 was indicated by bands at about 7.4, 9.2 and 11.85 μ, SiF_4 by absorption at about 9.75 μ, and N_2F_2 (inactive *) by absorption at about 10.05 μ and 10.2 μ.

b. Experimental Results

The results of the experimental program, summarized in Table 1, demonstrate that despite the changes to Haller's procedure that were made to facilitate the work, the preparation and collection of azine fluoride is still a nerve-wracking experience.

There was no infrared spectral evidence (Runs 2 through 6) for the formation of new gaseous species upon passage of the azine fluoride mixture through solid potassium, rubidium, and cesium fluorides at ambient temperature. Minor changes in the relative amounts of FN_3 and N_2F_2 may have occurred, but this was not definitely established.

In several instances (Runs 3, 5, 6, and 13) weight-increases in the metal fluoride tubes occurred upon passage of the azine fluoride reaction mixture. This weight increase was much higher (Runs 7 and 8) when collection in Freon was avoided. In none of these cases, however, could the uptake of an oxidizing species be detected when potassium iodide test reagent with starch solution was subsequently employed. Examination of infrared spectrum (Run 6) indicated little, if any, absorption of SiF_4 occurs under these conditions.**

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* R. H. Sanborn, J. Chem. Phys., 33, 1855 (1960).

** It has been reported that sodium fluoride absorbs SiF_4 only very slowly below 200°C; V. A. Yattov and I. G. Ruiss, J. Appl. Chem. (USSR), 5, 332 (1932).

However, the absorbed material was acidic and its gram equivalent weight was determined by titration (Runs 8 and 13) in three cases to be 22.4, 20.2, and 20.3 (HF-20.0).

On two occasions (Runs 12 and 13) the amount of oxidizing material was determined (by iodimetry) before and after passage through the metal fluoride. The results indicate a minimum recovery of 94 to 96%.

c. Conclusion

These experimental results make it apparent that there has been no formation of a new species or even uptake of azine fluoride by potassium, rubidium, and cesium fluorides at ambient temperature. Past and present observations of weight-increases in the treated metal fluorides probably resulted from absorption of HF. Only one earlier observation* has not been explained by the present work - the explosion encountered with a sample of KF first exposed to FN_3 and then heated to 80°C. During the present program, one sample of metal fluoride, obtained from a sequence in which a weight increase occurred (Run 8), was rapidly heated to 120°C without evidence of concomitant decomposition or explosion. From personal communication with Dr. Haller, it has been ascertained that no unusual steps were taken by him in preparing the potassium fluoride employed in the earlier work so that, if a surface effect is involved, it is not possible to readily reproduce the necessary conditions.

The failure to note absorption by metal fluorides of gaseous azine fluoride under the experimental conditions employed does not, of course, constitute proof for the non-existence of the desired N_3F_2 anion. It could, for example, be reasonably argued that like the absorption of gaseous SiF_4 to form M_2SiF_6, the absorption of FN_3 is too slow at ambient temperature to be observed; attempts to test the postulate would unfortunately be frustrated by the thermal instability of FN_3, which prevents a study into a temperature range much above ambient. Recognizing such limitations, it is nonetheless felt that the earlier observations upon which the present experimental program was

*J. F. Haller, Dissertation, Cornell University Library, Ithaca, New York.

was undertaken have been clarified with the result that there is no longer any evidence that can be considered as supporting the hypothesis of anion formation.

3. Experimental

A diagram of the apparatus is shown in Figure 41.

a. Alkali Metal Fluorides

The alkali fluorides were prepared for use by washing the reagent-grade anhydrous salts with spectrograde carbon tetrachloride in a dry box and drying the solids in air at 125°C overnight, followed by cooling in the dry box.

b. Azine Fluoride

Hydrazoic acid was generated over a 45-min period by heating to 125°C a mixture of 98.5 g of stearic acid and 15.5 g of recrystallized sodium azide; under these conditions the generation of HN_3 was not complete. The HN_3 was continuously swept from the generator by a helium stream (ca. 4 liters/hour). The dilute HN_3 and fluorine (ca. 1-2 liters/hour), also diluted with helium (ca. 2-3 liters/hour), were mixed in a reaction coil, prepared from 20 feet of 1/4-in.-OD stainless steel tubing, maintained at about 25°C. The exit product stream was passed first through a trap maintained at 0°C and then a calibrated trap, at -80°C, containing 300 ml of Freon-11.

III. SUMMARY

A. REACTIONS OF DIFLUORAMINE

The reaction of acetylenes with difluoramine in the presence of $BF_3 \cdot H_3PO_4$ gave gem-difluoramines, ketones, α-fluorodifluoramines, and Beckman rearrangement products of the intermediate vinyl difluoramines.

The reaction of vinylidene chloride with difluoramine in fuming sulfuric acid gave 1,1-dichloro-1-(difluoramino)ethane, 1-chloro-1,1-bis(difluoramino)ethane, and another compound, for which preliminary evidence suggests the structure, 1,1,1-tris(difluoramino)ethane.

The reaction of 1,1-dichloro-1-butene-3-one with difluoramine in fuming sulfuric acid gave 1,1-dichloro-3,3-bis(difluoramino)-1-butene. Increasing the relative amount of the ketone in the reaction gave N-[2,2-dichloro-1,2-bis(difluoramino)ethyl]acetamide.

The reaction of 2-chloro-2-penten-4-one with difluoramine gave 2,2,4,4-tetrakis(difluoramino)pentane, 2-chloro-2,4,4-tris(difluoramino)pentane and 2-chloro-3,4,4-tris(difluoramino)pentane.

The reactivity of gem-difluoramines with a variety of acids, bases and reducing agents was studied. Ethyl 5,5-bis(difluoramino)hexanoate was converted to the corresponding alcohol, acid and isocyanate. 5,5,5-Trinitro-2,2-bis(difluoramino)pentane was reduced to 5,5-dinitro-2,2-bis(difluoramino)pentane, which, in turn was hydrolyzed to 4,4-bis(difluoramino)pentanoic acid.

1-Methyl-1-(difluoramino)cyclohexane and cyclohexyl difluoramine reacted with acids to give ring-expanded NF cations. The reduction of these starting materials was also studied.

B. AQUEOUS FLUORINATION

The aqueous fluorination of primary amides gave the corresponding amines by Hofmann rearrangement. In the case of cyclohexanecarboxamide, the intermediate isocyanate was isolated.

The fluorination N-2-hydroxyethylacetamide gave β-difluoraminoethyl acetate. Transesterification with methanol gave β-difluoraminoethanol.

Ethyl difluoraminoacetate was obtained by the fluorination of ethyl N-carbomethoxyglycine. Ethyl difluoraminoacetate, ethyl cyanoformate and ethyl N,N-difluoro-hydantoate were obtained from ethyl hydantoate.

The fluorination of lactams gave ω-difluoraminocarboxylic acids and N-fluorolactams. Attempts to use the latter as fluorinating agents were unsuccessful.

The aqueous fluorination of N,N'-dicyclohexylurea and of cyclohexylurea gave cyclohexyl isocyanate. The latter reaction also gave difluoraminocyclohexane and N,N-difluorocyclohexylurea.

The yield of 1,3-bis(difluoramino)propane from the fluorination of the dicarbamates was improved by substituting the methyl for the ethyl derivative previously used. The fluorination of ethyl cyclopentylcarbamate and ethyl cyclohexylcarbamate gave the cycloalkyl difluoramines.

The fluorination of ethyl azodicarboxylate and ethyl hydrazodicarboxylate gave tricarbethoxyhydrazine.

The reaction of methyl carbamate with phosphorus pentoxide gave N,N'-difluoroallophanate.

C. FLUORAMMONIUM SALTS

The reaction of ethyl N-fluorocarbamate with sulfuric acid gave a fluorammonium salt containing carbonaceous anions. The reaction of this carbamate with methanesulfonic acid gave fluorammonium methanesulfonate. Some unsuccessful attempts were made to metathesize this salt to the perchlorate.

D. REACTIONS OF AZINE FLUORIDE

No evidence of a complex was observed between alkali metal fluorides and azine fluoride. Weigh increases noted when mixtures arising from azine fluoride preparations are passed through metal fluorides have been related to the presence of hydrogen fluoride.

IV. CONCLUSIONS AND RECOMMENDATIONS

A. The replacement of halogens by difluoramine has been shown to be a promising method for preparing highly energetic NF compounds. The method merits further study and exploitation.

B. A number of common synthetic organic transformations have been carried out successfully without interference from gem-difluoramino groups. Applications to situations requiring superior stability toward chemical environment is apparent.

C. Isolated difluoramino groups have been shown to be sensitive to strong acids, giving Beckmann rearrangements. Additional study is warranted both in terms of theoretical interest and for the potential limitations imposed for propellant ingredients.

D. The aqueous fluorination of primary amides results in the Hofmann rearrangement of the unstable monofluoro-intermediates. Although of theoretical interest, additional study in this area is not an immediate need.

E. The aqueous fluorination of carbamates is a versatile method for the preparation of alkyl difluoramines. The insolubility of intermediates, a current limitation to general application, appears solvable by the use of mixed solvents. Additional study along the latter lines is needed.

F. A stable fluorammonium salt, the methane sulfonate, has been prepared, thereby demonstrating the stability of the cation under appropriate conditions. Attempts to introduce an oxidizing anion through metathesis have not been encouraging. The alternate approach of decomposition of the fluorocarbamate in the presence of perchloric acid has been more encouraging and requires further investigation.

G. No evidence has been obtained for the formation of a complex from the reaction of azine fluoride and alkali fluorides. Additional effort to obtain the $N_3F_2^{\ominus}$ anion by this means can not be justified.

V. PERSONNEL

The experimental work was performed by K. Baum, J. M. Cavallo, F. J. Gerhart, E. D. Gilley, A. F. Graefe, V. Grakauskas, M. P. Mascari, L. Pendelton, A. H. Remanick, and R. K. Robeson. Analytical support was provided by C. L. Deuel and H. W. Pust (Gas Chromatography), K. Inouye (Microanalyses), D. I. Matson (IR) and H. Nelson (NMR, Operation and Interpretation).

TABLE 1

SUMMARY OF AZINE FLUORIDE REACTIONS

Run No.	Handling of FN_3	Salt Cells Present	Results
1	Collected in Freon-11, -80°C	None	a. An explosion occurred in HN_3 generator during run. b. Freon-11 solution contained 40.8 milliequivalents of oxidizing material.
2		One Cell, KF	a. Freon-11 solution contained 38.3 meq. of oxidizing material. b. IR spectrum indicated presence of FN_3 in vapor at inlet to KF cell. c. Explosion destroyed Freon trap during the warming.
3		2 Cells in Series, KF	a. 18.7 meq. of oxidizing material in Freon solution. b. IR spectrum indicates FN_3 in vapor. c. Total weight gain of two KF cells was 0.1115 grams. d. No oxidizing properties for contents of KF cells with KI test reagent.
4		2 Cells in Series, KF	Explosion in Freon trap during collection.
5	Collected in Freon-11, -80°C	2 Cells in Series, KF	a. 22.5 meq. of oxidizing material in Freon solution. b. IR spectrum demonstrates presence of FN_3 in vapor at inlet to KF cells. c. Total weight increase of KF cells was 21 meq. d. KI test for presence of oxidizing material in KF cells was negative.

TABLE 1 (cont.)

Run No.	Handling of FN_3	Salt Cells Present	Results
6	Collected in Freon-11, -80°C	2 Cells in Series, One RbF, One CsF	a. 41.2 meq. of oxidizing material collected in Freon. b. IR spectra indicate presence of FN_3 both at inlet and outlet of salt cells. c. Weight gains of cells, ca. 1 mg. per cell. d. KI test negative on cell contents.
7	Product Stream Passed Directly through Metal Fluoride Cells	One Cell, KF	a. Weight gain of KF cell was 150 mg. b. No oxidizing species in KF cell. c. Explosion of HN_3 generator terminated run.
8	Product Stream Passed Directly through Metal Fluoride Cells	3 Cells in Series, KF	a. Weight gains of cells were 441 mg, 68 mg, and 44 mg, respectively. b. Contents of first cell did not oxidize iodide reagent. Base titration of contents of cell indicate gram equivalent weight of 22.4 for absorbed material. c. Crystals from 2nd cell were heated rapidly to 120°C without evidence of decomposition or explosion. d. Base titration of contents of 3rd cell indicate absorbed material had gram-equivalent weight of 20.2.
9	Collected in Freon at -80°C	2 Cells in Series, KF	Explosion in Freon trap terminated run.
10	Collected in Freon at -80°C	2 Cells in Series, KF	Explosion in HN_3 generator.

TABLE 1 (cont.)

Run No.	Handling of FN_3	Salt Cells Present	Results
11	Collected in Freon at -80°C	2 Cells in Series, KF	Leak in system terminated run
12	Collected in Freon at -80°C	One Cell, KF	a. 31.8 meq. of oxidizing material collected in Freon.
			b. 30.4 meq. (95.2%) of oxidizing material recovered after passage through KF cell.
			c. KF cell weight increase was 2 mg.
			d. No iodide test with content of KF cell.
13	Collected in Freon at -80°C	2 Cells in Series, One NaF, One KF	a. 30.4 meq. of oxidizing material collected in Freon.
			b. 28.7 meq. (94.2%) of oxidizing material recovered after passage through salt cells.
			c. Weight gain of NaF cell was 249 mg. Gram - equivalent weight of absorbed material by base titration was 20.2.
			d. KF cell weight increase was 0.3 mg. - iodide test was negative.

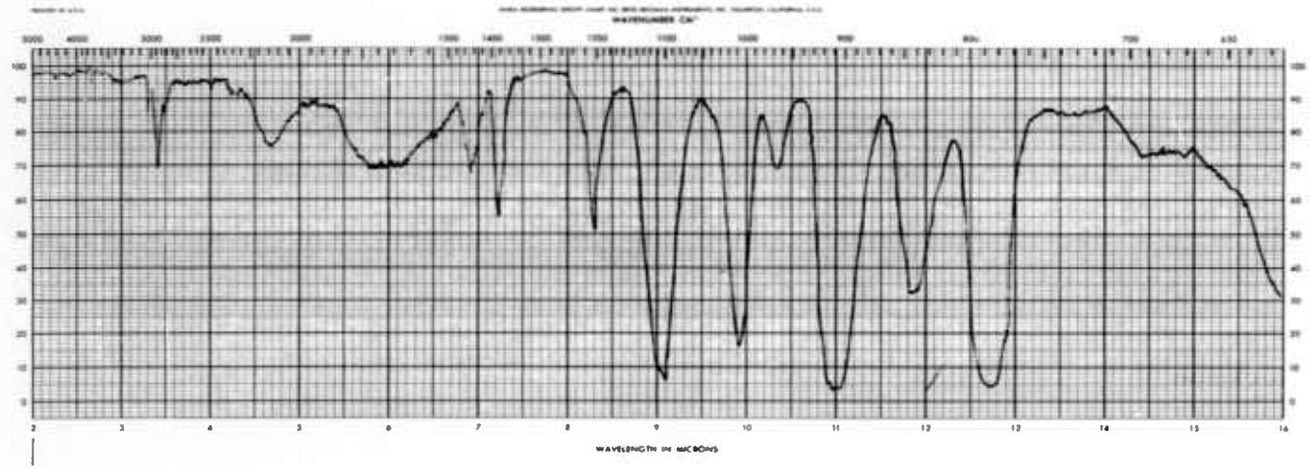

Fig. 1 Infrared Spectrum of 1,1-Dichloro-1-(difluoramino)ethane

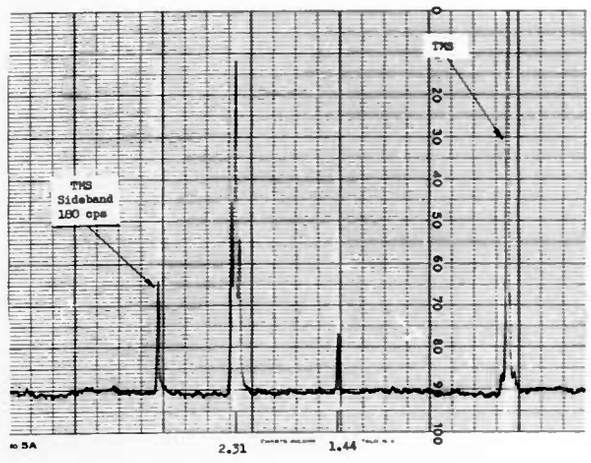

Fig. 2 Proton NMR Spectrum of 1,1-Dichloro-1-(difluoramino)ethane

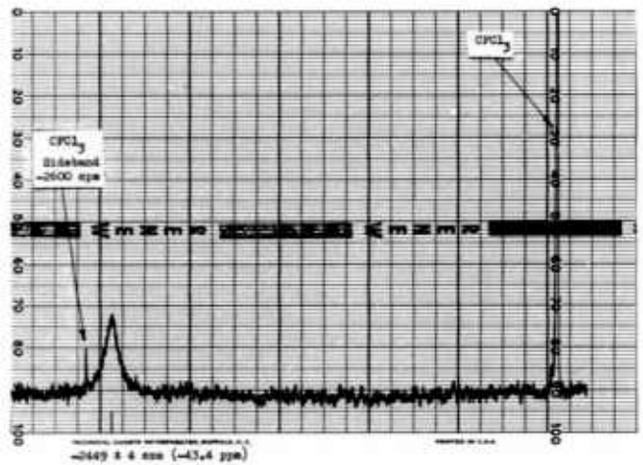

Fig. 3 Fluorine NMR Spectrum of 1,1-Dichloro-1-(difluoramino)ethane

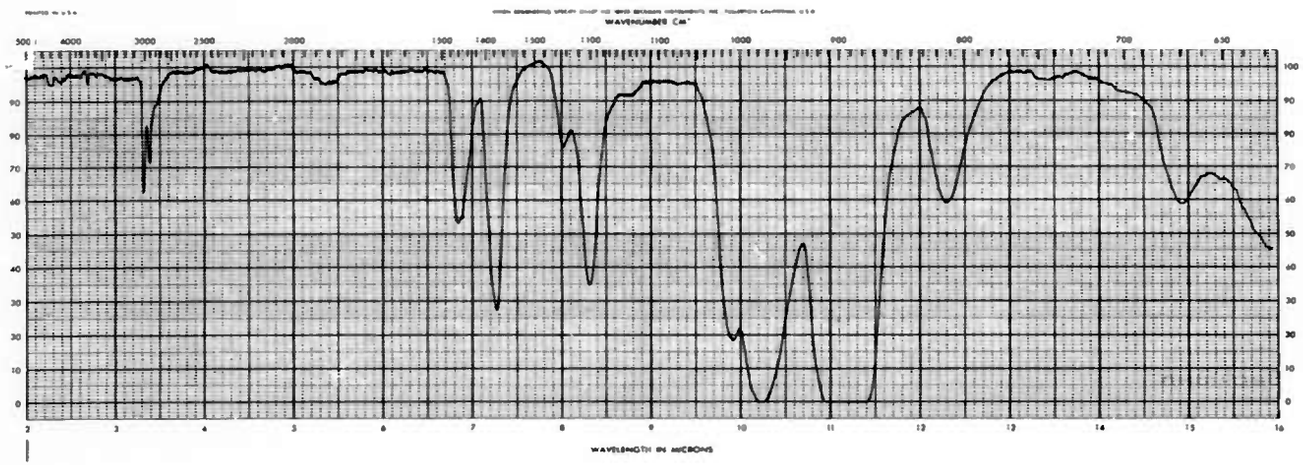

Fig. 4 Infrared Spectrum of 1-Chloro-1,1-bis(difluoramino)ethane

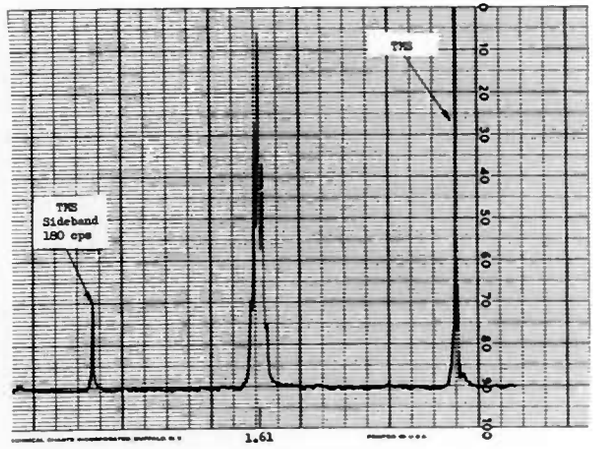

Fig. 5 Proton NMR Spectrum of 1-Chloro-1,1-bis(difluoramino)ethane

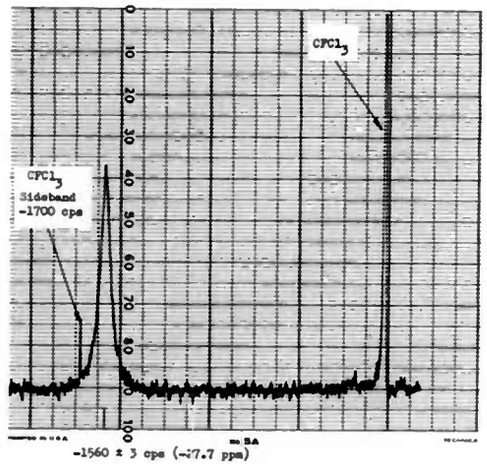

Fig. 6 Fluorine NMR Spectrum of 1-Chloro-1,1-bis(difluoramino)ethane

Figures 4, 5, and 6

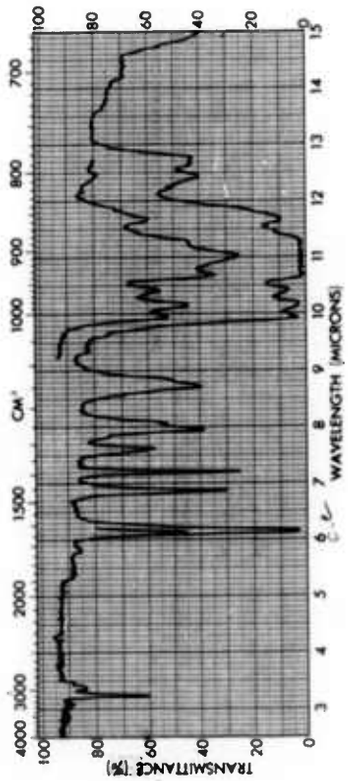

Fig. 7 Infrared Spectrum of 1,1-Dichloro-3,3-bis(difluoramino)-1-butene

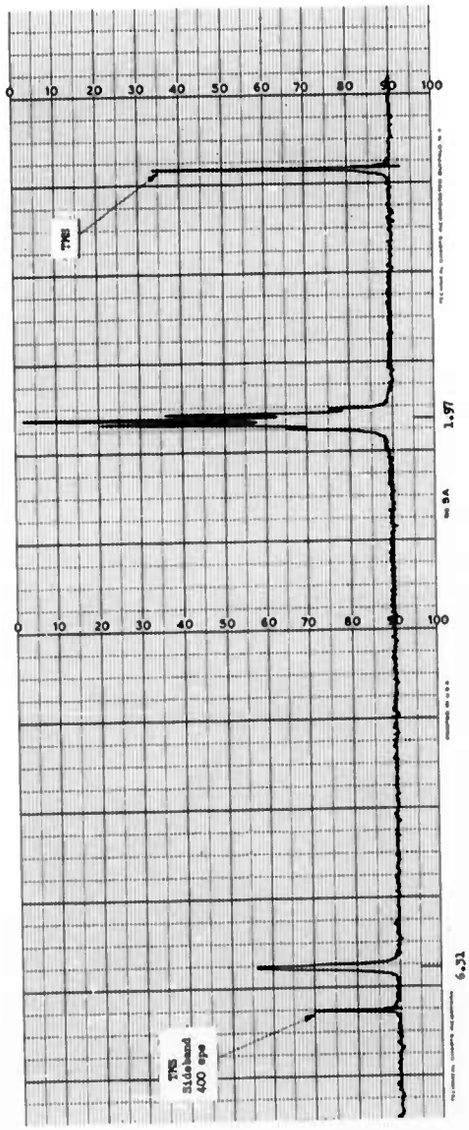

Fig. 8 Proton NMR Spectrum of 1,1-Dichloro-3,3-bis(difluoramino)-1-butene

Figures 7 and 8

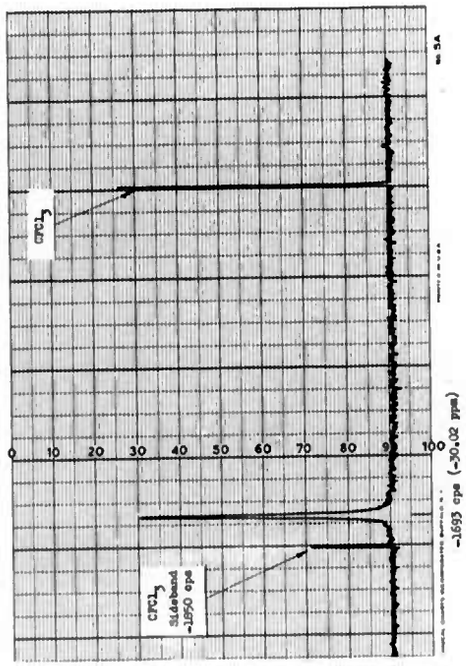

Fig. 9 Fluorine NMR Spectrum of 1.1-Dichloro-3.3-bis(difluoramino)-1-butene

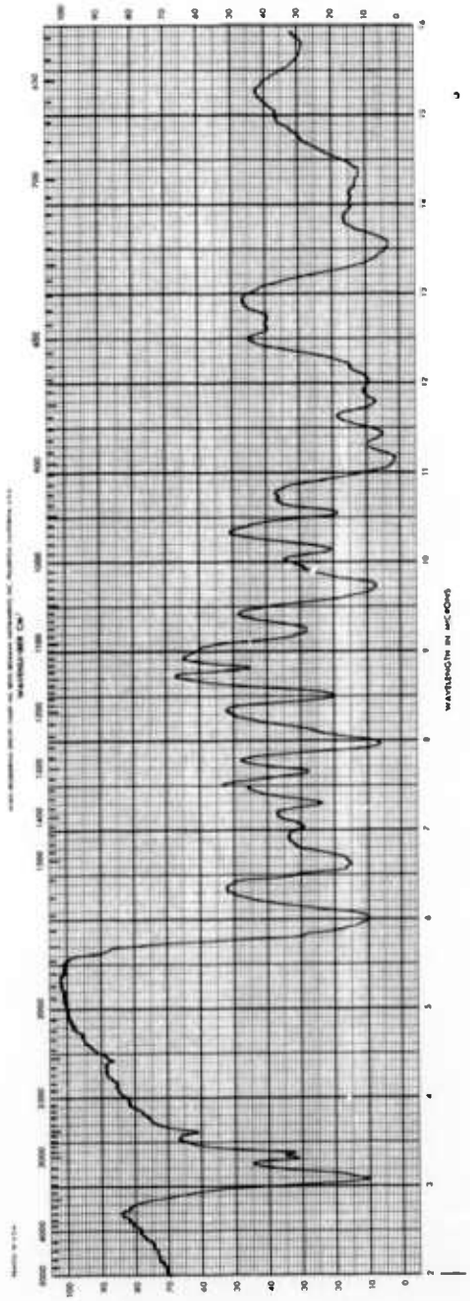

Fig. 10 Infrared Spectrum of N-[2,2-dichloro-1,2-bis(difluoramino)ethyl] acetamide

Figures 9 and 10

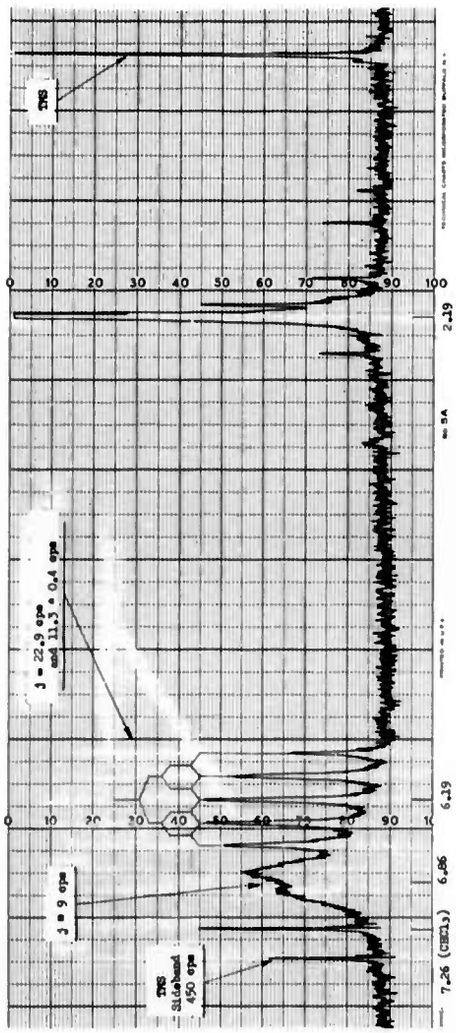

Fig. 11 Proton NMR Spectrum of N-[2,2-dichloro-1,2-bis(difluoramino)ethyl] acetamide

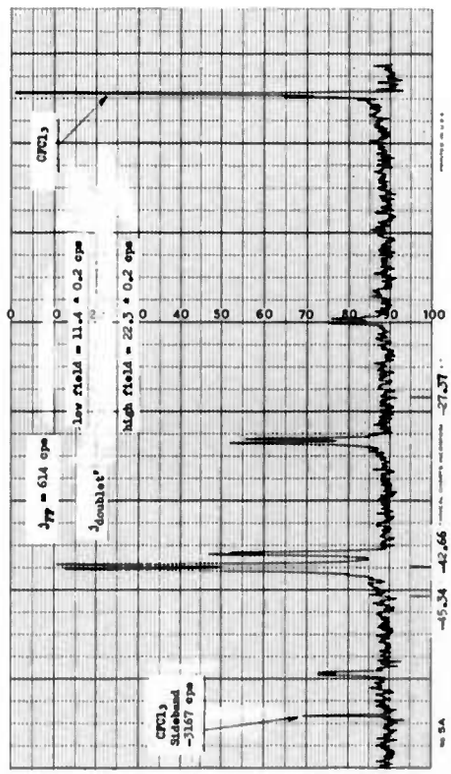

Fig. 12 Fluorine NMR Spectrum of N-[2,2-dichloro-1,2-bis(difluoramino)ethyl] acetamide

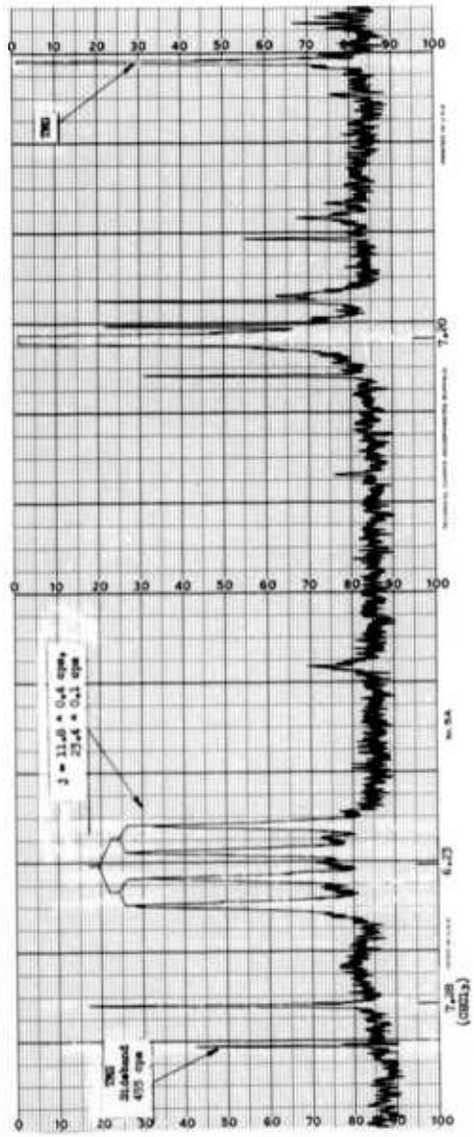

Fig. 13 Proton NMR Spectrum of N-[2,2-dichloro-1,2-bis(difluoramino)ethyl]acetamide, Deuterated

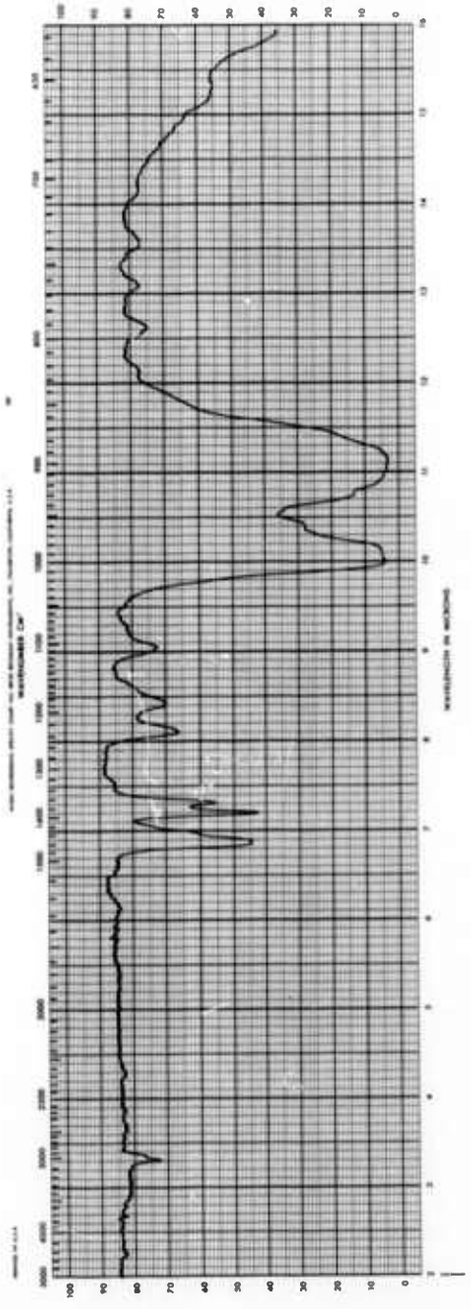

Fig. 14 Infrared Spectrum of 2,2,4,4-Tetrakis(difluoramino)pentane

Figures 13 and 14

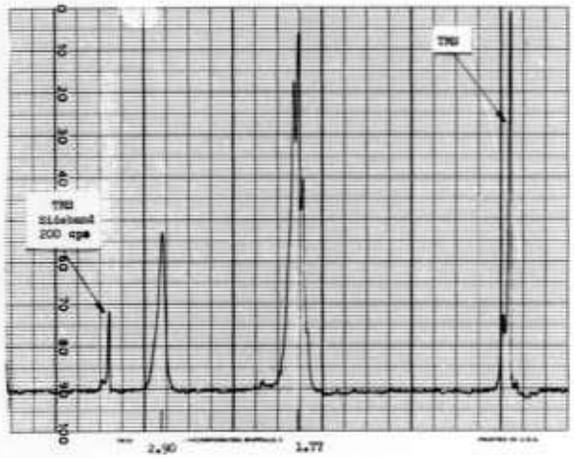

Fig. 15 Proton NMR Spectrum of 2,2,4,4-Tetrakis(difluoramino)pentane

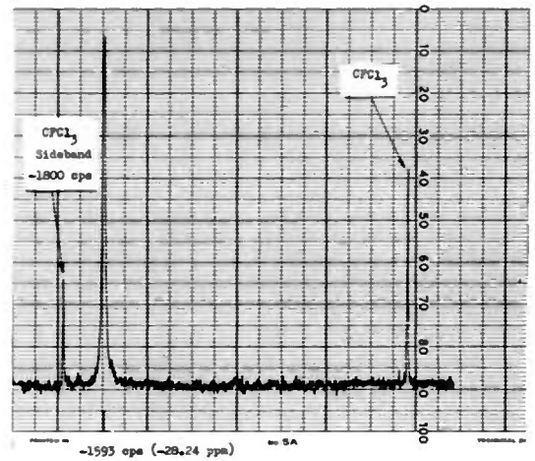

Fig. 16 Fluorine NMR Spectrum of 2,2,4,4-Tetrakis(difluoramino)pentane

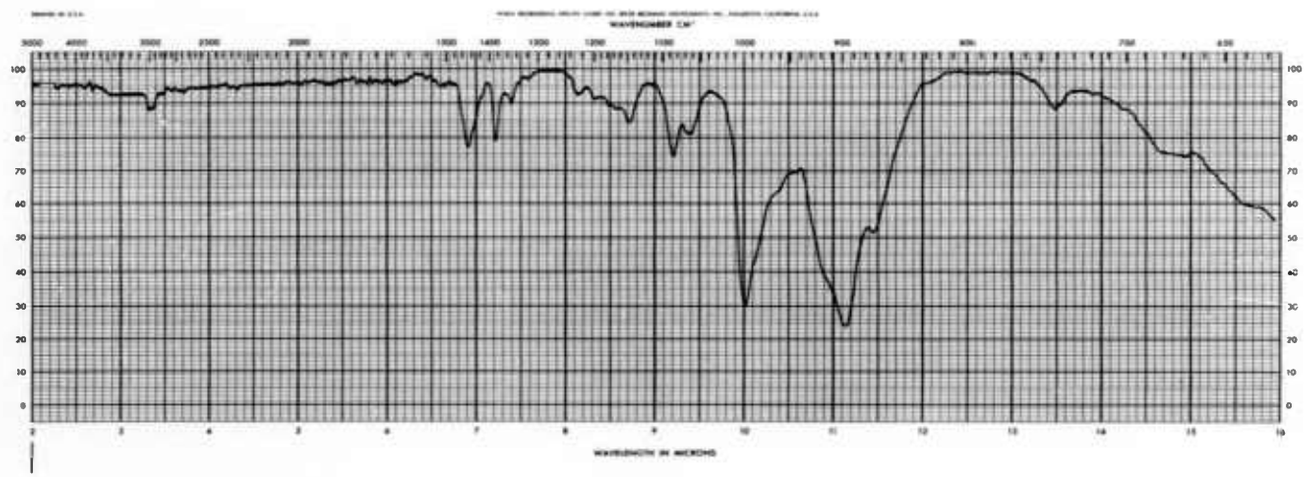

Fig. 17 Infrared Spectrum of 2-Chloro-2,4,4-tris(difluoramino)pentane

Figures 15,16, and 17

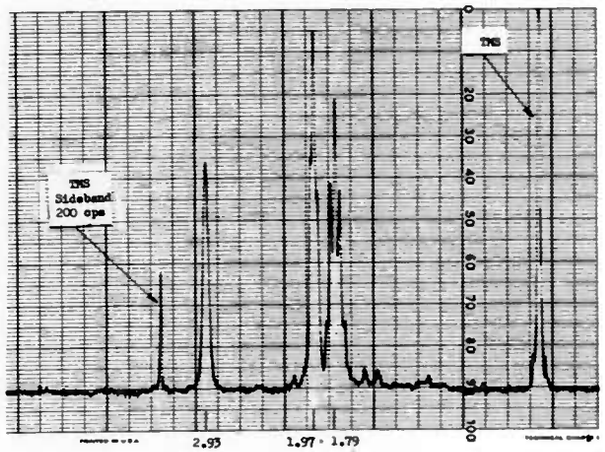

Fig. 18 Proton NMR Spectrum of 2-Chloro-2,4,4-tris (difluoramino)pentane

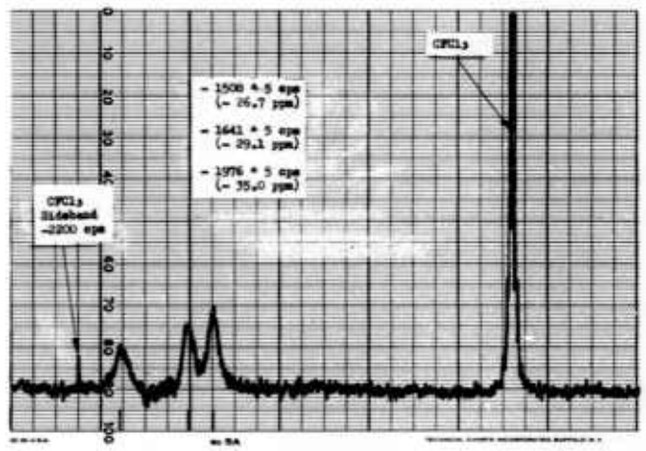

Fig. 19 Fluorine NMR Spectrum of 2-Chloro-2,4,4-tris(difluoramino)pentane

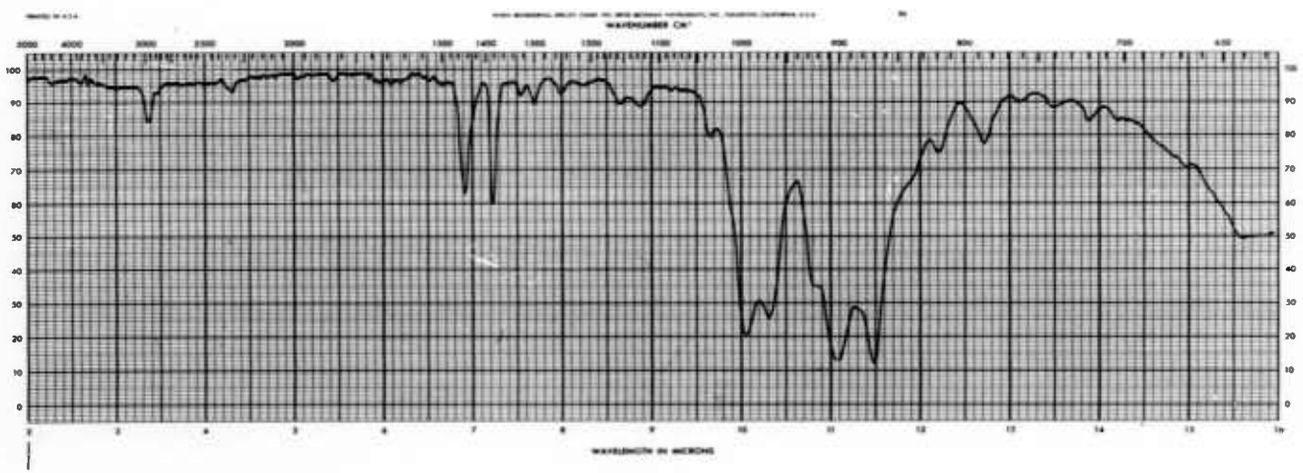

Fig. 20 Infrared Spectrum of 2-Chloro-3,4,4-tris(difluoramino)pentane

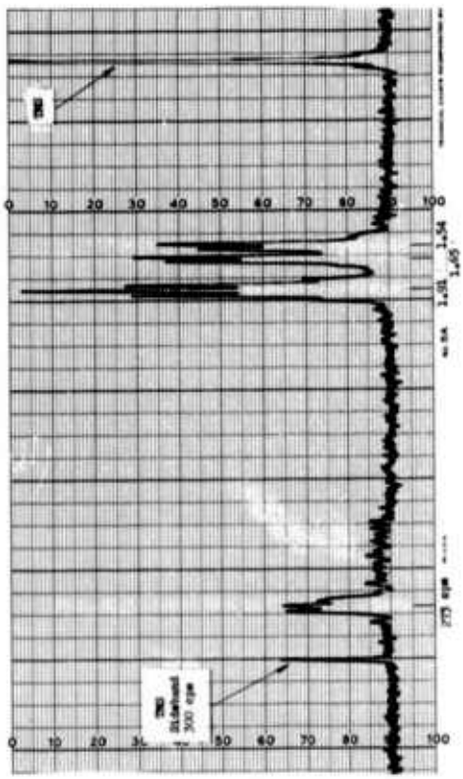

Fig. 21 Proton NMR Spectrum of 2-Chloro-3,4,4-tris(difluoramino)pentane

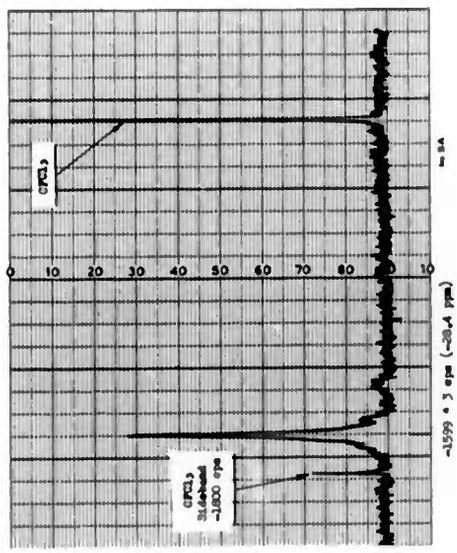

Fig. 22 Fluorine NMR Spectrum of 2-Chloro-3,4,4-tris(difluoramino)pentane

Figures 21 and 22

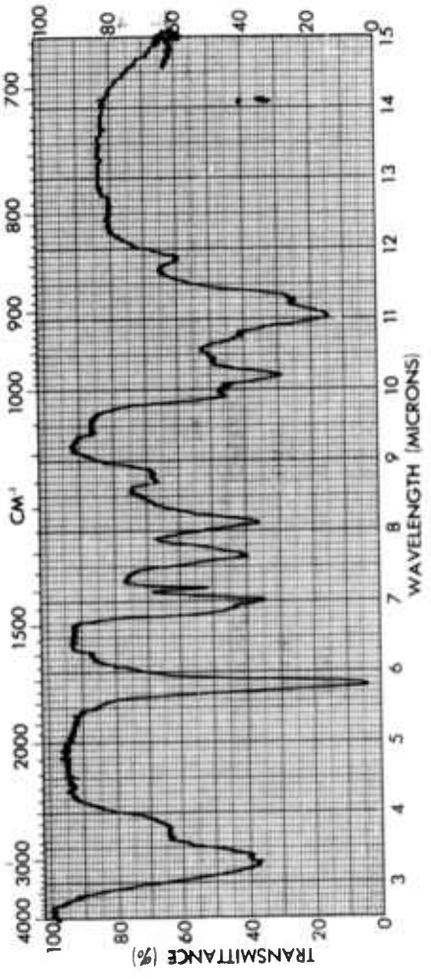

Fig. 23 Infrared Spectrum of 4,4-bis(difluoramino)pentanoic Acid.

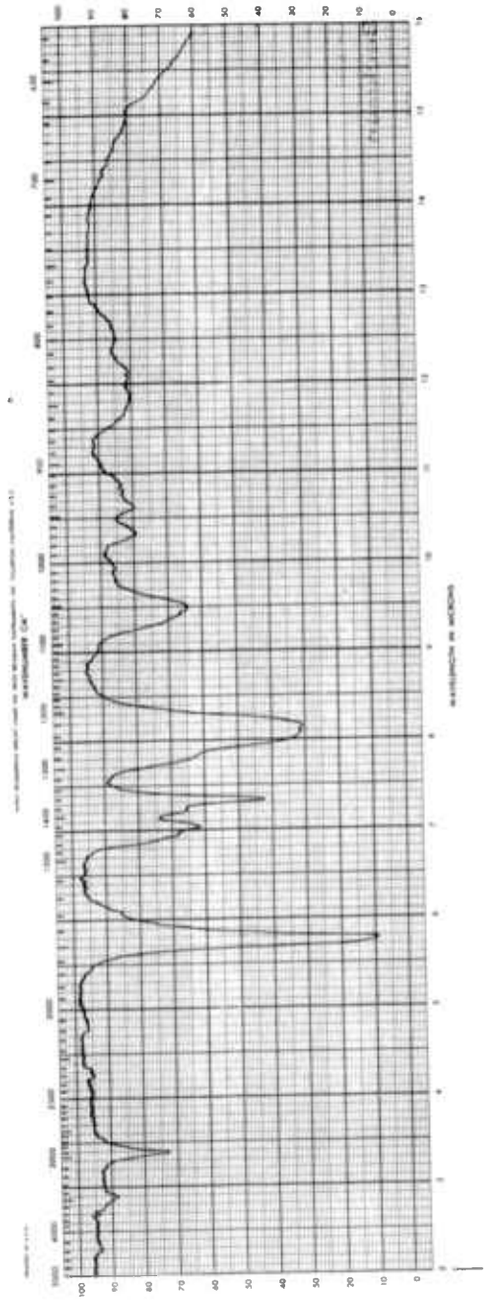

Fig. 24 Infrared Spectrum of β-Difluoraminoethyl Acetate

Figures 23 and 24

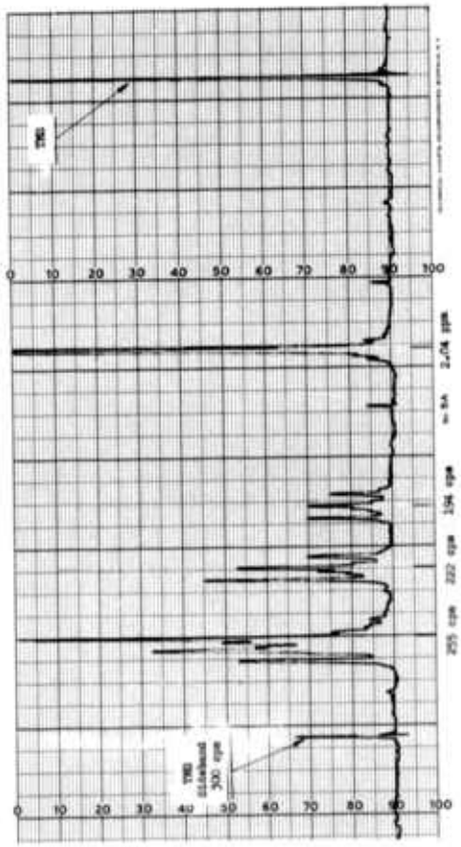

Fig. 25 Proton NMR Spectrum of β-Difluoraminoethyl Acetate

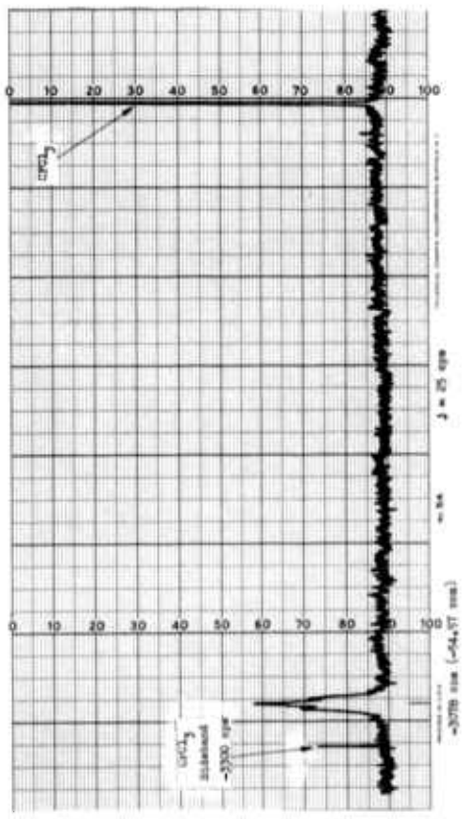

Fig. 26 Fluorine NMR Spectrum of β-Difluoraminoethyl Acetate

Figures 25 and 26

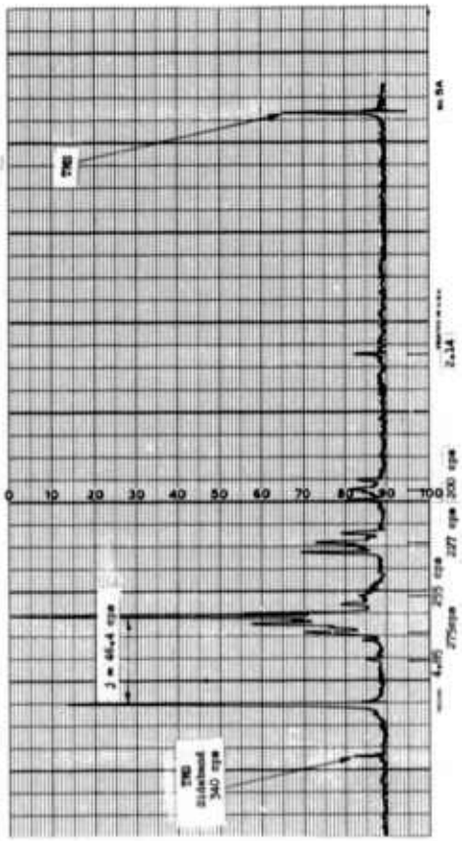

Fig. 27 Proton NMR Spectrum of β-Difluoraminoethyl Fluoroacetate

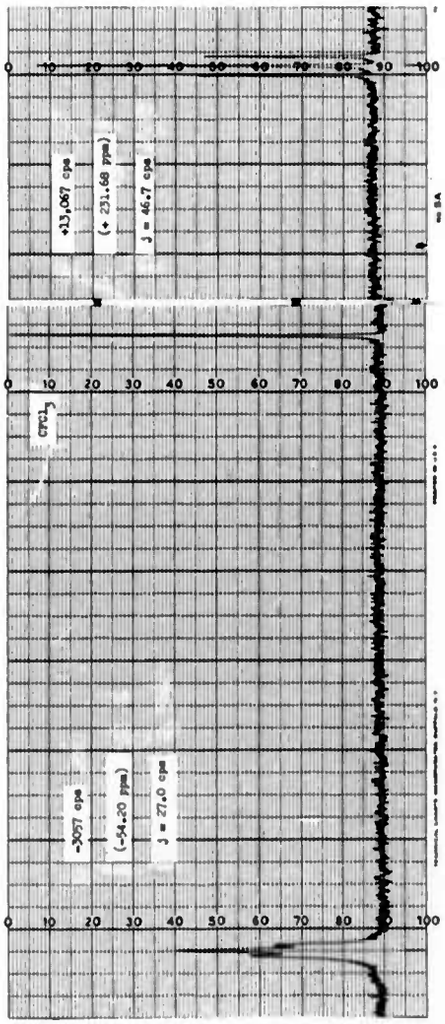

Fig. 28 Fluorine NMR Spectrum of β-Difluoraminoethyl Fluoroacetate

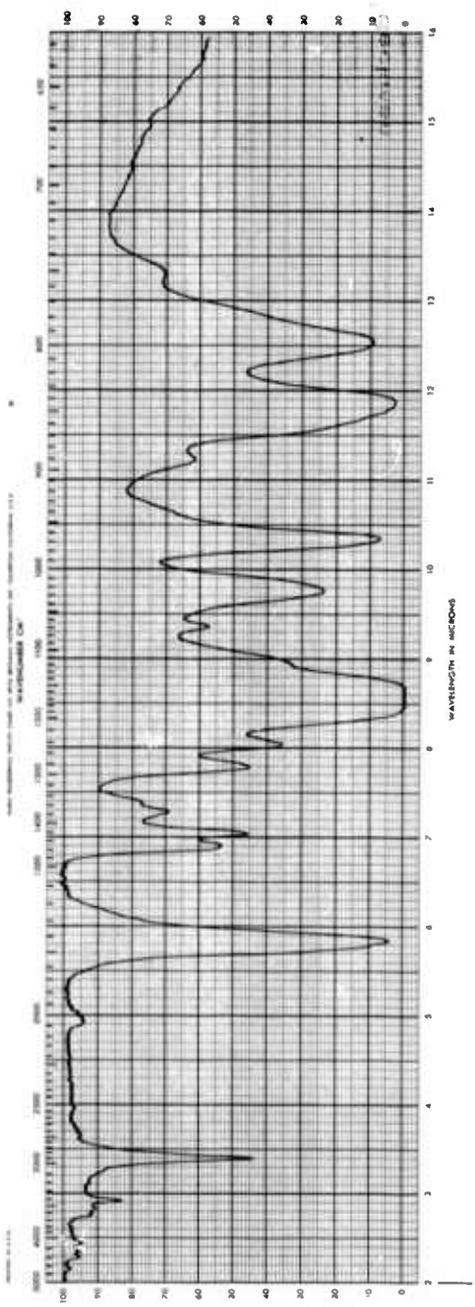

Fig. 29 Infrared Spectrum of β-Difluoraminoethyl Formate

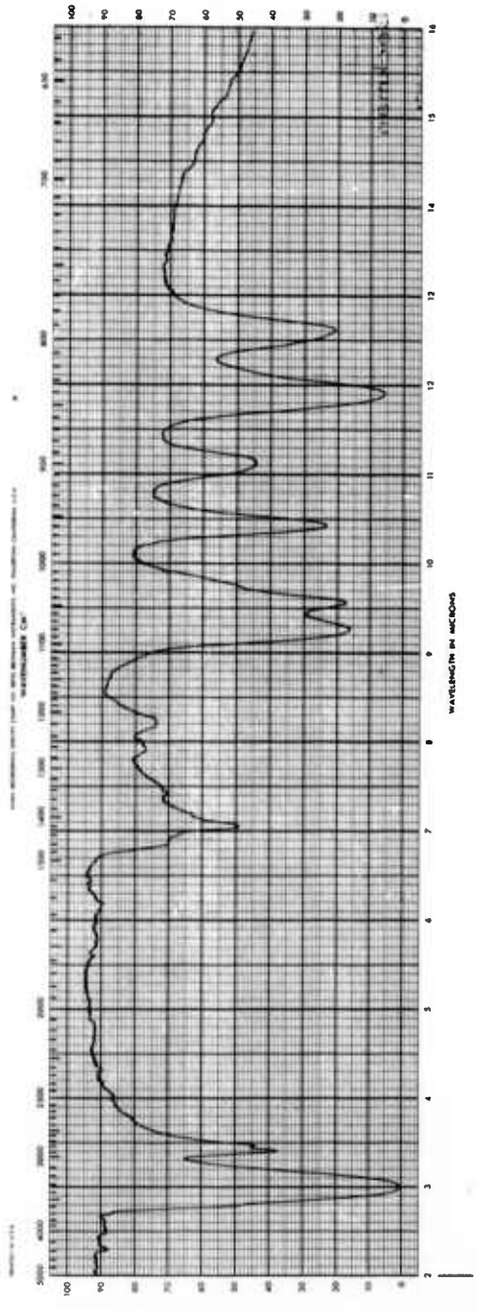

Fig. 30 Infrared Spectrum of β-Difluoraminoethanol

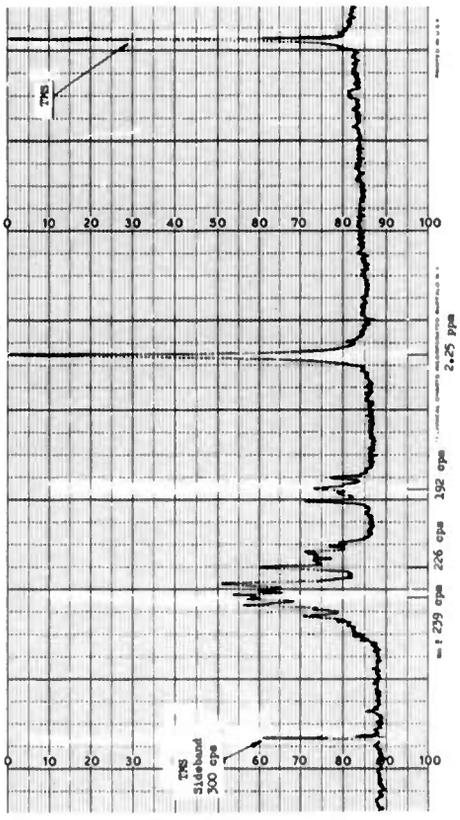

Fig. 31 Proton NMR Spectrum of β-Difluoraminoethanol

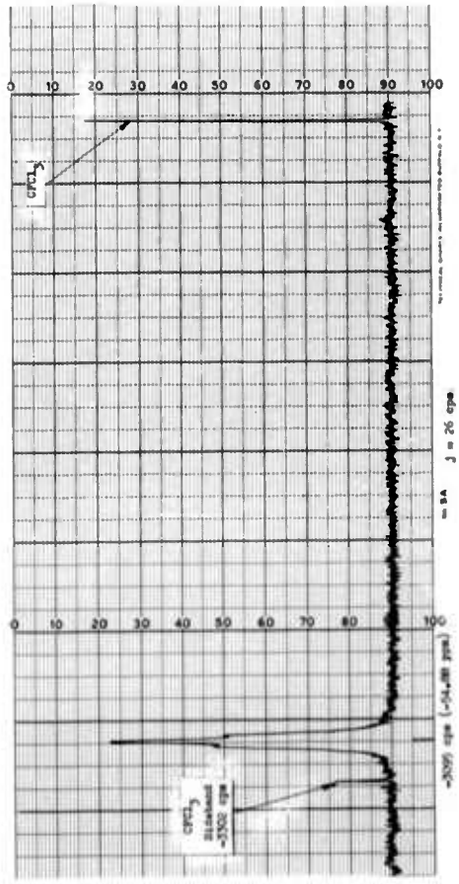

Fig. 32 Fluorine NMR Spectrum of β-Difluoraminoethanol

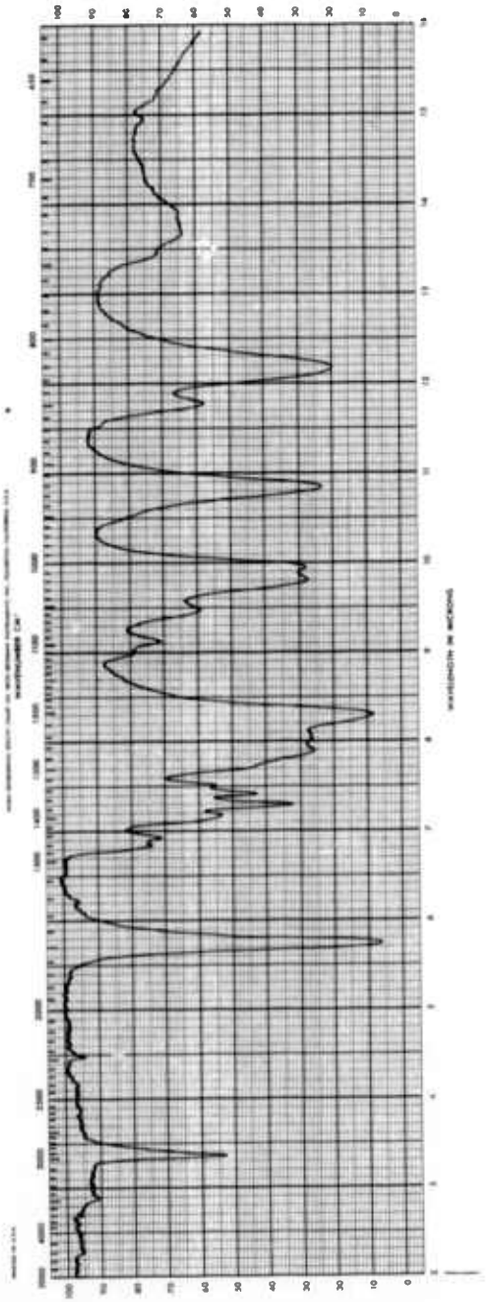

Fig. 33 Infrared Spectrum of Ethyl Difluoraminoacetate

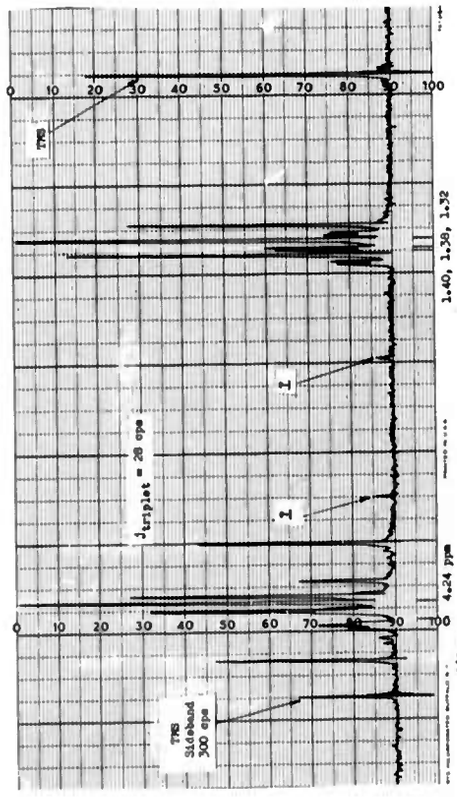

Fig. 34 Proton NMR Spectrum of Ethyl Difluoraminoacetate

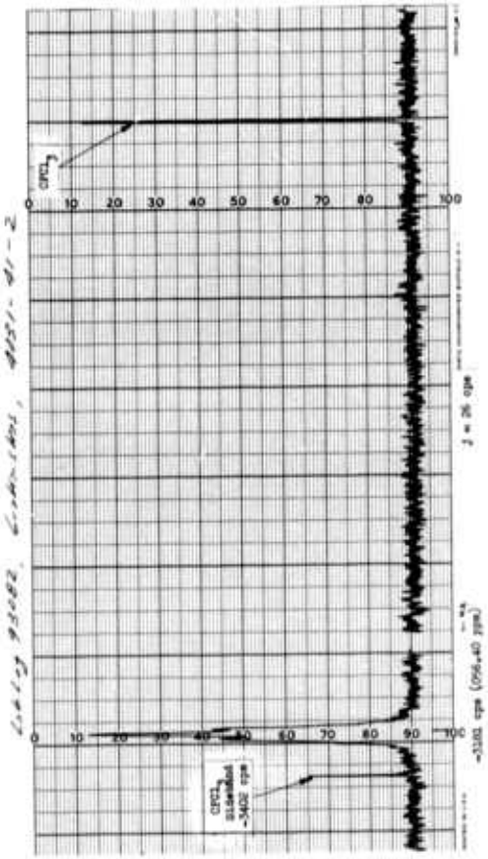

Fig. 35 Fluorine NMR Spectrum of Ethyl Difluoraminoacetate

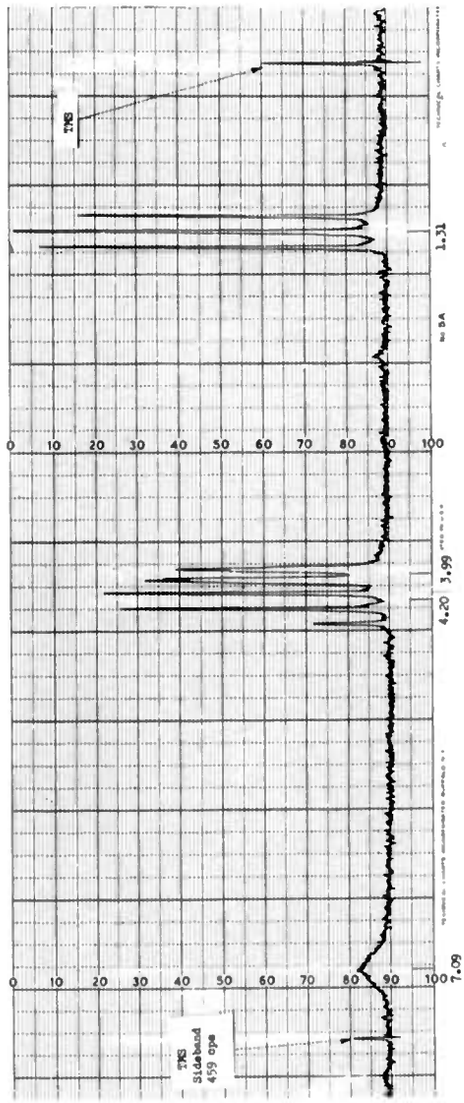

Fig. 36 Proton NMR Spectrum of Ethyl N,N-Difluorohydantoate

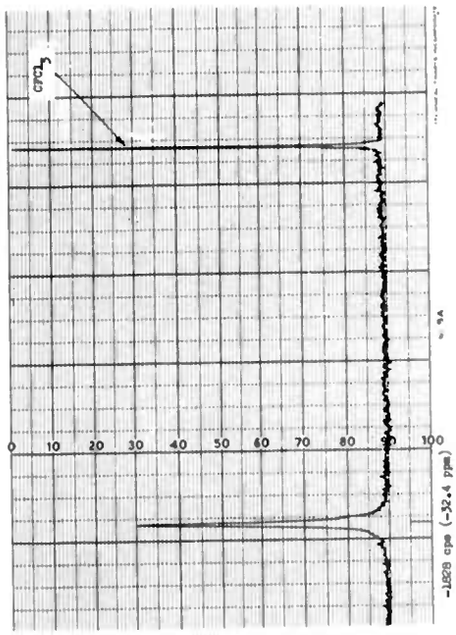

Fig. 37 Fluorine NMR Spectrum of Ethyl N,N-Difluorohydantoate

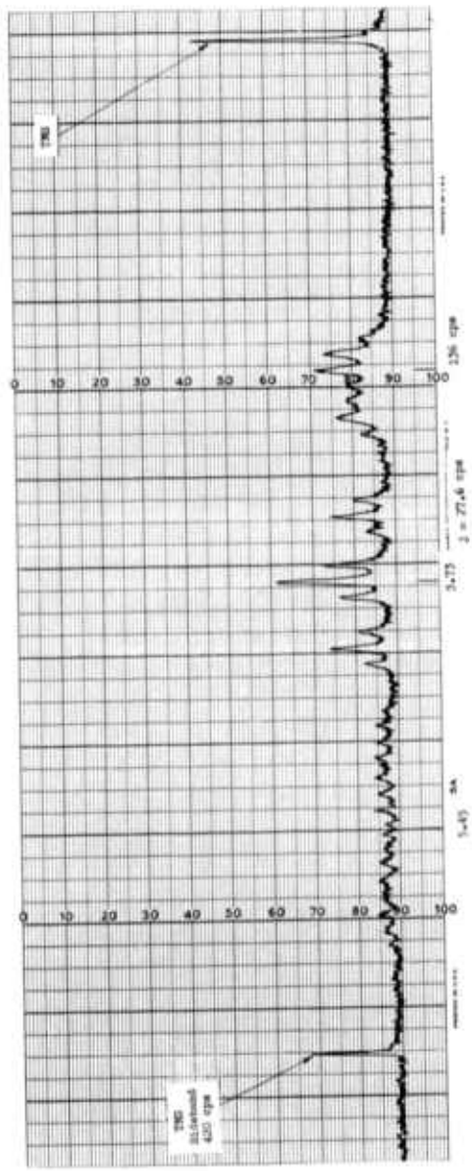

Fig. 38 Proton NMR Spectrum of 1,3-Bis(difluoramino)-1-fluoropropane

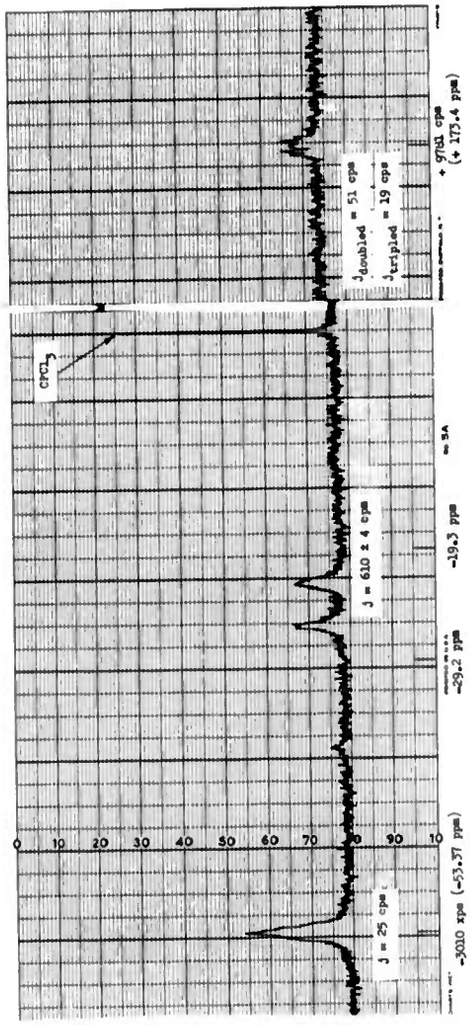

Fig. 39 Fluorine NMR Spectrum of 1,3-Bis(difluoramino)-1-fluoropropane

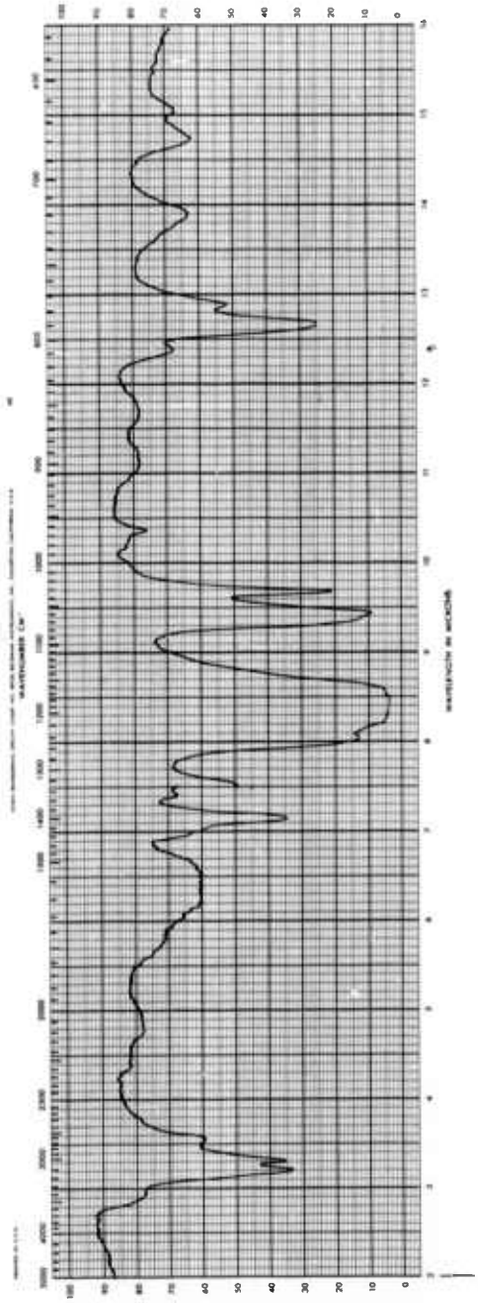

Fig. 40 Infrared Spectrum of Fluorammonium Methanesulfonate

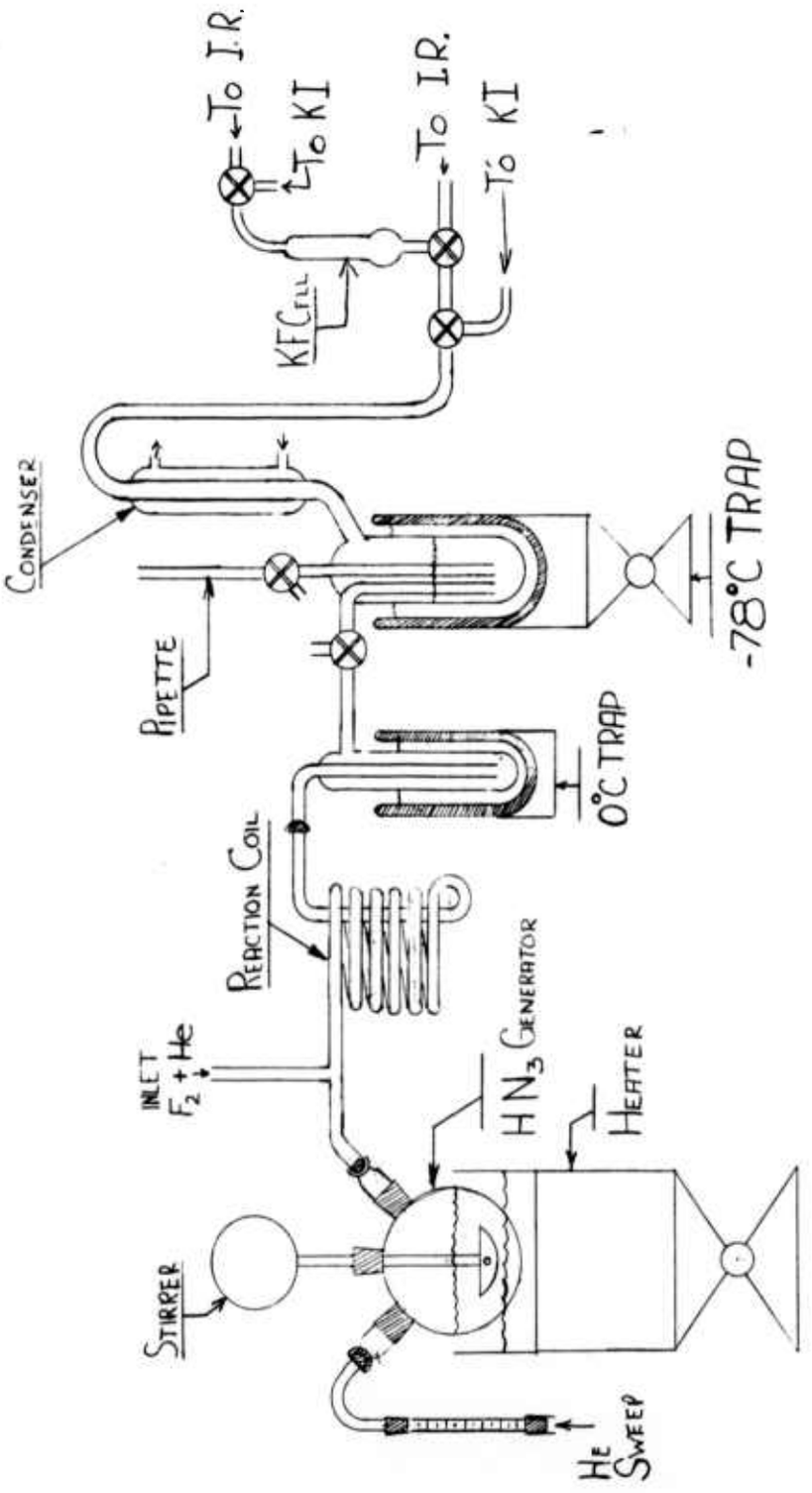

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Fig. 41 Azine Fluoride Apparatus

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